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COLLABORATIVE STUDY OF METHOD 10 - REFERENCE METHOD FOR DETERMINATION OF CARBON MONOXIDE EMISSIONS FROM STATIONARY SOURCES. REPORT OF TESTING

Paul C. Constant, Jr., et al

Midwest Research Institute

Prepared for:

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January 1975

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The collaborators submitted tentative readings after each test and later sent MRI their final results, which included the original recorder charts. MRI checked the collaborators' results and then statistically analyzed the collaborators' results.

The collaborators' results from sampling the CO boiler stack were analyzed to determine the precision of the method and the standard gas results were used to determine the accuracy of the method.

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by

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January 1975

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FOREWORD

The collaborative study of "Method 10 - Determination of Carbon Monoxide Emissions from Stationary Sources" was conducted under Tasks 3 and 5 of EPA Contract No. 68-02-1098, which is Midwest Research Institute Project No. 3814-C, entitled "Standardization of Stationary Sources Emission Measurement Methods." Midwest Research Institute acquired a sampling location and field facilities for the test, selected seven collaborators to perform sampling according to its plan of test, retrieved field data and analysis results from the collaborators, statistically analyzed the results, and prepared this two-volume report.

This volume, Volume I, of the report of test, summarizes MRI's and the collaborators' activities. It just presents those activities that were necessary in preparing for the field test--selection of the site, design, construction and checkout at the field site of a manifold sampling apparatus needed for the collaborative test, selection of the collaborators and the experimental design. This preliminary work is then followed by a discussion of the field test, a summary of the results of the collaborators, MRI's statistical analyses of the collaborators' results, conclusions and recommendations.

Volume II of this report contains results of the collaborators that were submitted to MRI.

The seven organizations that participated under subcontract to Midwest Research Institute (MRI) in the test of Method 10 are Coors Spectro-Chemical Company, Golden, Colorado; Ecology Audits (subsidiary of Core Laboratories, Inc.), Dallas, Texas; Entropy Environmentalists, Inc., Research Triangle Park, North Carolina; Environmental Triple S, St. Louis, Missouri; Interpoll Incorporated, St. Paul, Minnesota; Scott Environmental Technology, Inc., Plumsteadville, Pennsylvania; and TRW, McLean, Virginia.

The following individuals of these organizations are acknowledged for their participation in the collaborative test: Mr. Dan Briggs of Coors Spectro-Chemical Company, Mr. Michael Hartman of TRW, Mr. Sam Humphries of Ecology Audits, Inc., Mr. Maynard Johnson of Scott Environmental Technology, Inc., Mr. Roger Johnson of Interpoll Incorporated, Mr. Bill McClarence of Environmental Triple S Company, and Mr. Joe Schiappa of Entropy Environmentalists.

Special acknowledgments are made to the El Dorado Refinery of the American Petrofina of Texas, which is located in El Dorado, Kansas, and to Mr. Leon Randolph, Superintendent of the El Dorado Refinery for providing the test location and for the excellent cooperation and courtesies that were extended MRI and the collaborators; to Dr. John B. Clements, Chief, Methods Standardization and Performance Evaluation Branch, National Environmental Research Center, Environmental Protection Agency, and Mr. M. Rodney Midgett, Government Project Officer, Methods Standardization and Performance Evaluation Branch, for their valuable suggestions in planning and reporting; and to the National Bureau of Standards (NBS) for supplying the tanks of standard gases.

The MRI program is being conducted under the management and technical supervision of Mr. Paul C. Constant, Jr., Head, Environmental Measurements Section of MRI's Physical Sciences Division, who is program manager. Dr. George Scheil was MRI's field supervisor at El Dorado, Kansas, during the 2-week test. Mr. Michael Sharp was responsible for the experimental design and statistical analyses.

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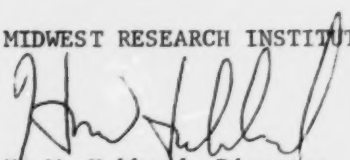

H. M. Hubbard, Director
Physical Sciences Division

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SUMMARY

A collaborative test was conducted by MRI at the El Dorado Refinery of American Petrofina of Texas during 3 to 14 June 1974. Seven organizations participated in the test of "Method 10 - Determination of Carbon Monoxide Emissions from Stationary Sources." All collaborators sampled simultaneously using the integrated bag method. The sampling manifold was connected to the CO boiler stack of the fluid catalytic cracking unit. All runs were of 60 min duration. Each collaborator obtained four samples per day--two in the morning and two in the afternoon. Sixteen runs were made at each of two CO levels. MRI had an NDIR operating in the continuous mode during each run to monitor the CO concentration. Each collaborator analyzed six cylinders of CO in nitrogen which had been certified by the National Bureau of Standards.

The collaborators submitted tentative readings after each test and later sent to MRI their final results, which included the original recorder charts. MRI checked the collaborators' results and then statistically analyzed the collaborators' results.

The collaborators' results from sampling the CO boiler stack were analyzed to determine the precision of the method and the standard gas results were used to determine the accuracy of the method.

Pertinent statistical results from this collaborative test are:

1. For the field data:

   - The within-collaborator standard deviation (σ_e) is about 13 ppm.*

   - The collaborator-collaborator standard deviation (σ_c) is about 25 ppm.

---

* The quantity actually estimated from the analysis of variance is $\sigma_e^2 + \sigma_{LC}^2$ (35 ppm). Indirect methods decompose this sum and result in σ_e = 13 ppm.

- In general, the collaborators' calibration curves are suitably parallel but this is not true for all collaborators.

2. For the standards:

- The within-collaborator standard deviation (σ_e) is about 4.5 ppm.

- The collaborator-collaborator standard deviation (σ_c) is about 22 ppm.

- Although the average bias is quite low (average overall levels, 7 ppm), the bias definitely varies according to the CO level. The bias is, in general, larger at the lower CO levels (up to 24 ppm when CO = 239 ppm), but not all collaborators have parallel bias versus concentration curves.

The principal conclusions that are drawn from the results of this collaborative test are:

1. Method 10 as executed in this collaborative test will produce results with only moderate accuracy of ± 87 ppm (2σ) on the average.

2. The procedure as written in Method 10 is not adequate because:

a. The Ascarite weight gain method for measuring CO_2 content on the sample is subject to large errors due to the difficulty of measuring the small weight change obtained compared to the weight of the impinger plus the Ascarite;

b. The use of an impinger or bottle for the Ascarite trap causes great difficulties because the Ascarite tends to form a dense, solid plug in and around the glass inlet tube which, in turn, blocks the flow of the gas after a period of time;

c. Most commercial NDIR instruments have a significant amount of curvature in the calibration curves, and many of the collaborators did not adequately correct for this nonlinearity of response; and

d. Some calibration gas suppliers provide certificates of analysis that show errors of as much as 30% when compared with standard gases.

Based upon the conclusions that have been drawn from the results of this collaborative test, it is recommended that Method 10 be revised to cover the following points:

1. All mention of the CO_2 determination by weight gain of the Ascarite gas scrubber should be deleted. Carbon dioxide should be done by Method 3 (Orsat-type analysis) of the Federal Register.

2. The use of an impinger or bottle type of silica gel and Ascarite gas scrubber should be deleted. Sections of a flexible plastic pipe, capped at the ends, should be used instead. A minimum internal diameter of 2.5 cm is recommended to prevent blockage.

3. More explicit instructions on correcting for nonlinear response of the instruments are desirable.

4. Analysis procedures of some calibration gas suppliers are clearly inadequate. Reliable calibration gases might require NBS certification or a requirement that gas suppliers follow specific guidelines in their analysis of calibration gases.

SECTION I

INTRODUCTION

The Methods Standardization and Performance Evaluation Branch, National Environmental Research Center of the Environmental Protection Agency (EPA) is engaged in a program to evaluate methods, recommended and promulgated by EPA, for the measurement of pollutant emissions from stationary sources. Midwest Research Institute (MRI) is working for EPA under Contract No. 68-02-1098 to provide data on the reliability and bias of the methods.

To achieve its objective, MRI plans and executes a collaborative test and evaluation for each method submitted to it by EPA. Briefly, in the execution of a collaborative test, MRI performs an in-house evaluation of the method (which could range from a paper evaluation, such as was the case for this test, to a ruggedness test), provides sampling locations and facilities relative to the test and analysis involved, coordinates the collaborative test, retrieves field data and results of the collaborators' chemical analyses of their samples, statistically analyzes results received from the collaborators, and reports results to EPA.

The work activities described above were performed by MRI under Tasks 3 and 5 of Contract No. 68-02-1098 on the collaborative test of "Method 10 - Reference Method for Determination of Carbon Monoxide Emissions from Stationary Sources," which is the subject of this report and is given on pages 9319 to 9321 of the Federal Register, 39, No. 47, Friday, 8 March 1974. (A copy of Method 10 is given in Appendix A.) These activities started in December 1973 with the review of the method. Following this the sampling manifold to be used by the collaborators in the field was designed and fabricated. Concurrently with this engineering effort, the El Dorado Refinery of American Petrofina of Texas was selected as the site for the collaborative test. The sampling manifold was then taken to the field site and tested. Seven collaborators

were selected for the field test which took place during 3 to 14 June 1974. During July, the collaborators submitted their results to MRI. These results were checked for errors and then statistically analyzed.

This report covers the collaborative test of Method 10 in the following order: Section II discusses the selection of the site, specifying the criteria followed and gives a description of the site that was selected for the test. Section III discusses the manifold sampling apparatus that was constructed by MRI and used by the collaborators. Section IV presents the experimental design of the test. Section V discusses the 2-week field test. Section VI summarizes the results of the test. Section VII gives the statistical analysis of the collaborators' results. Section VIII presents the major conclusions that were drawn from the results of the test. Section IX gives MRI's recommendations. Appendices comprise the write-up of Method 10, MRI's request for proposal that was sent to prospective collaborators, MRI's instructions to the collaborators, and the effects of deleted data from the principal analysis.

SECTION II

TEST SITE SELECTION AND DESCRIPTION

SITE SELECTION

The criteria for selection of a suitable refinery site are:

1. Sampling is to be done from the fluid catalytic cracking unit incinerator-waste heat boiler, commonly known as the CO boiler.

2. Carbon monoxide (CO) emissions must be controllable at or near the level of the EPA standard--500 ppm.

3. The site must provide sufficient area for testing and convenient access to the site must exist.

4. Necessary utilities, primarily electrical power, must be available.

5. Facility should be representative of refineries in the United States.

Sites were sought from several different petroleum companies. The El Dorado Refinery of American Petrofina of Texas, which is located in El Dorado, Kansas, approximately 180 miles from MRI, was the only one that accepted MRI's request. Although the carbon monoxide levels from the CO boiler at this facility are normally very low, approximately 30 ppm, refinery personnel believed that the desired levels of CO could be achieved without suffering a flameout and could be maintained at a level near 500 ppm for the testing.

SITE DESCRIPTION

While the El Dorado Refinery is a fairly small operation compared to most of the oil industry, no unusual conditions are known to exist

in the operation of the refinery that make it unrepresentative of normal industry practice. As shown in the next section of this report, CO levels of approximately 300 and 500 ppm are obtainable from the CO boiler stacks without causing an unstable condition in the FCCU.

The stack for the CO boiler at this site is approximately 100 ft high and is 54 in. in diameter at the top. A photograph of the stack is shown in Figure 1. The hot gases (500 to 900°F) from the CO boiler enter the stack from the inlet duct shown in the lower left of the photo approximately 20 ft from ground level. Four sampling ports are located approximately 60 ft from ground level. The stack is located adjacent to a refinery road and sufficient electrical power for the sampling equipment is available at the site. Ample ground area exists around the stack to accommodate seven collaborators and their sampling equipment.

Figure 1. Photo of CO boiler stack at El Dorado Refinery of American Petrofina of Texas, El Dorado, Kansas

Although there are adequately located sampling ports on the CO boiler stacks, it was not believed practical to place seven collaborators and all their equipment at an elevated sampling platform near these ports. The principal reasons are that each of the seven sampling probes would not necessarily be challenged with the same gas sample because of their different locations within the stack, and the collaborators would not be able to work effectively within the space limitations of a platform on top of scaffolding that would have to be erected. Consequently, MRI decided, with approval from EPA, to run a sampling line from one of the four existing ports to ground level and attach to it a sampling manifold from which each collaborator could effectively conduct sampling using Method 10 which would provide assurance that each collaborator's sampling apparatus would receive the same type gas sample.

SECTION III

CARBON MONOXIDE SAMPLING SYSTEM

DESIGN FACTORS

The initial field test setup is shown in Figure 2. The principal factors upon which this manifold system was designed to provide for simultaneous uniform sampling by a multiplicity of collaborators are:

1. Number of collaborators - maximum of 10.

2. Materials of construction - not critical; CO is not reactive or readily adsorbed or absorbed by most materials at moderate temperatures.

3. Gas stream flow rate - sufficient to assure each collaborator receives the same gas sample.

4. Manifold geometry - identical parallel branches and limited length for minimal pressure drop and gas flow transit time.

5. Water vapor - Method 10 does not require determination of water and each collaborator must have a water condenser at inlet of train. (Therefore, line from stack is unheated and provision for a drain made in system.)

6. Accessibility for sampling - ground-level sampling is far superior to sampling directly from stack.

CONSTRUCTION

All pipe in the sampling system from its intake point to the manifold is 1/2-in. stainless steel for heat and corrosion resistance, since these components are permanently mounted to the stack. The sample probe is mounted to a bulkhead fitting on the sample port. The

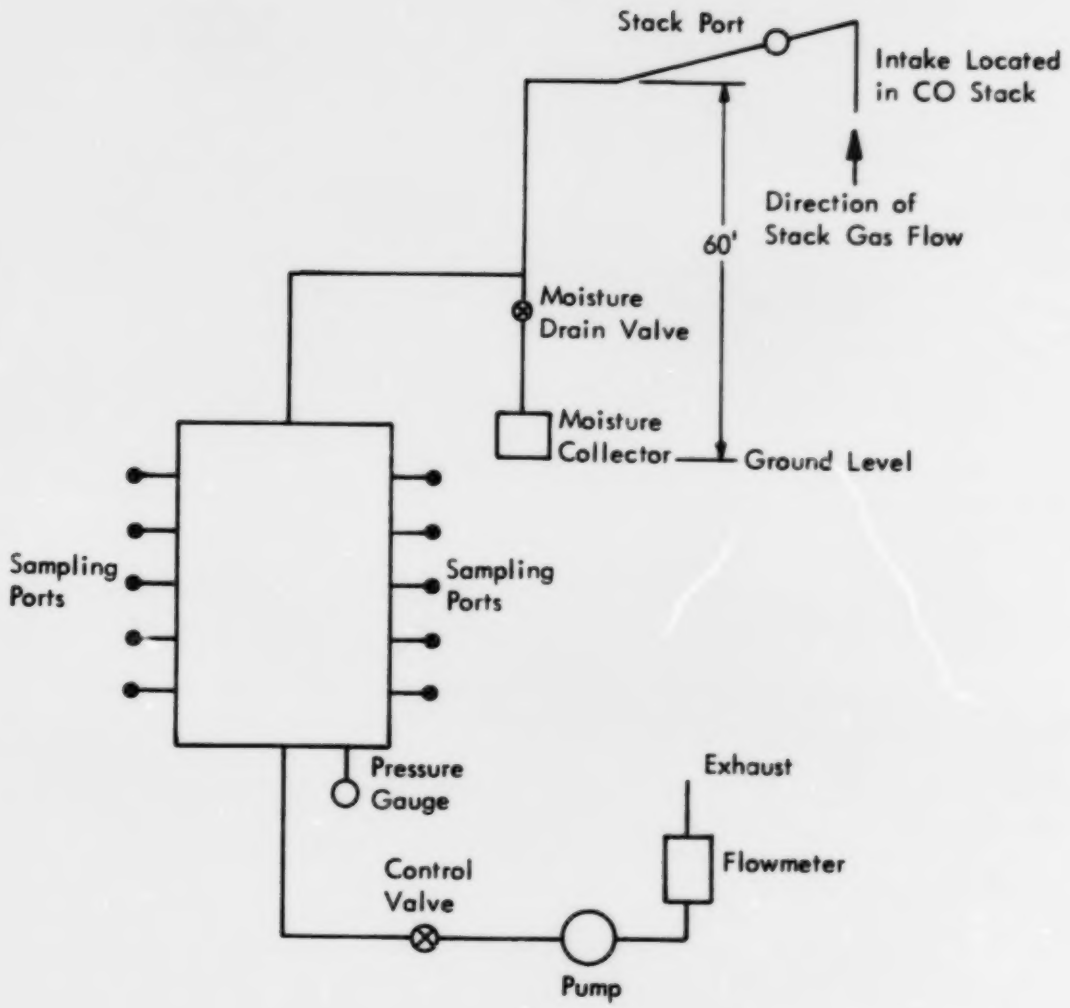


Figure 2. On site general test setup

probe extends to the center of the stack with a bend at the end and a 6-in. section of pipe pointed downward. From the exterior of the bulkhead fitting, the pipe runs outward 1 ft, bends around the stack to the steel supports shown in Figure 1 and then runs down to near ground level.

Photographs of the sampling manifold appear in Figure 3. Figures 4 and 5 show the different components of the sampling manifold in detail.

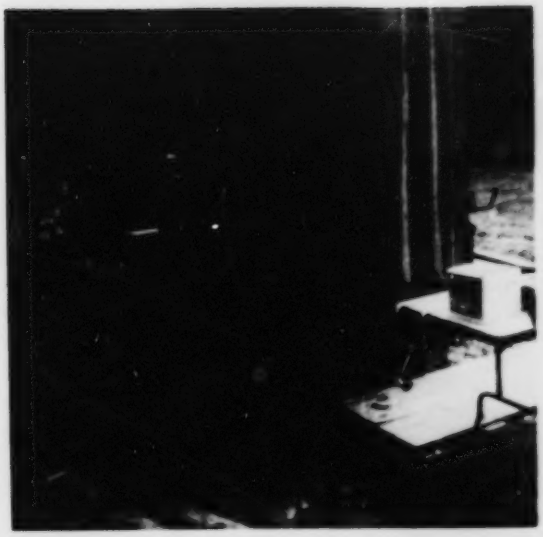
Figure 4 shows the sampling manifold and the rotameters for measuring flow rates in each branch of the manifold. All components in this section are 1/2-in. galvanized pipe and fittings. The sample outlet connections are 1/4-in. pipe nipples.

Figure 5 shows the pump and water condenser. The pump (A) is a GAST Model 0822-103-G27/X, carbon vane pump with a capacity of 7 ft^3/min. Control valve B regulates sample flow rate and the water trap (C) is a 32-oz, wide-mouth bottle with matching stopper, and (D) is a galvanized box with a 1/2-in. copper tubing coil inside. The water trap was not present in the preliminary test manifold.

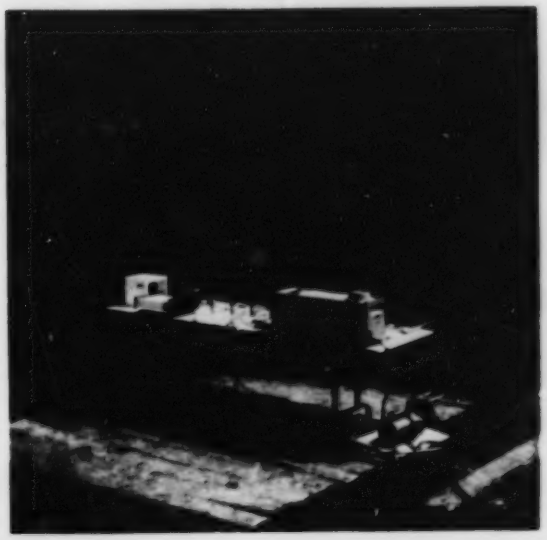
Figure 6 shows the NDIR used by MRI to monitor the CO level during each test. The filter (Part A of Figure 6) initially consisted of two separate plastic bottles with about 200 g of silica gel and 500 g of Ascarite, respectively. As explained in Section V, the impingers were replaced by the 1-in. diameter polyethylene tube shown. It should be noted that the needle valve had to be placed on the inlet side of the pump (Part B of Figure 6) rather than the outlet, as shown in Method 10. This was necessary because the pump is designed to operate with very little flow restriction on its exhaust side. Also the Millipore filter is needed to protect the nondispensive infrared (NDIR) analysis cells from dust contamination which degrades the signal response. All connections between the downpipe, manifold and pump were made with 1/2-in. galvanized pipe.

PRELIMINARY TESTING

In February 1974, MRI installed the sample pipe running from the stack to ground level and connected it to the sampling system shown in Figure 2 to determine if a CO level of 500 ppm could be safely reached and the CO concentration maintained at that level.



Photograph A. CO boiler stack with sample line on left side.



Photograph B. Sampling manifold with MRI's NDIR on table. CO boiler stack and cooling tower in background.

Photograph C. Sampling manifold on table. Pump under table, inlet line at far end of table.

Figure 3. Photographs of equipment set up for preliminary test

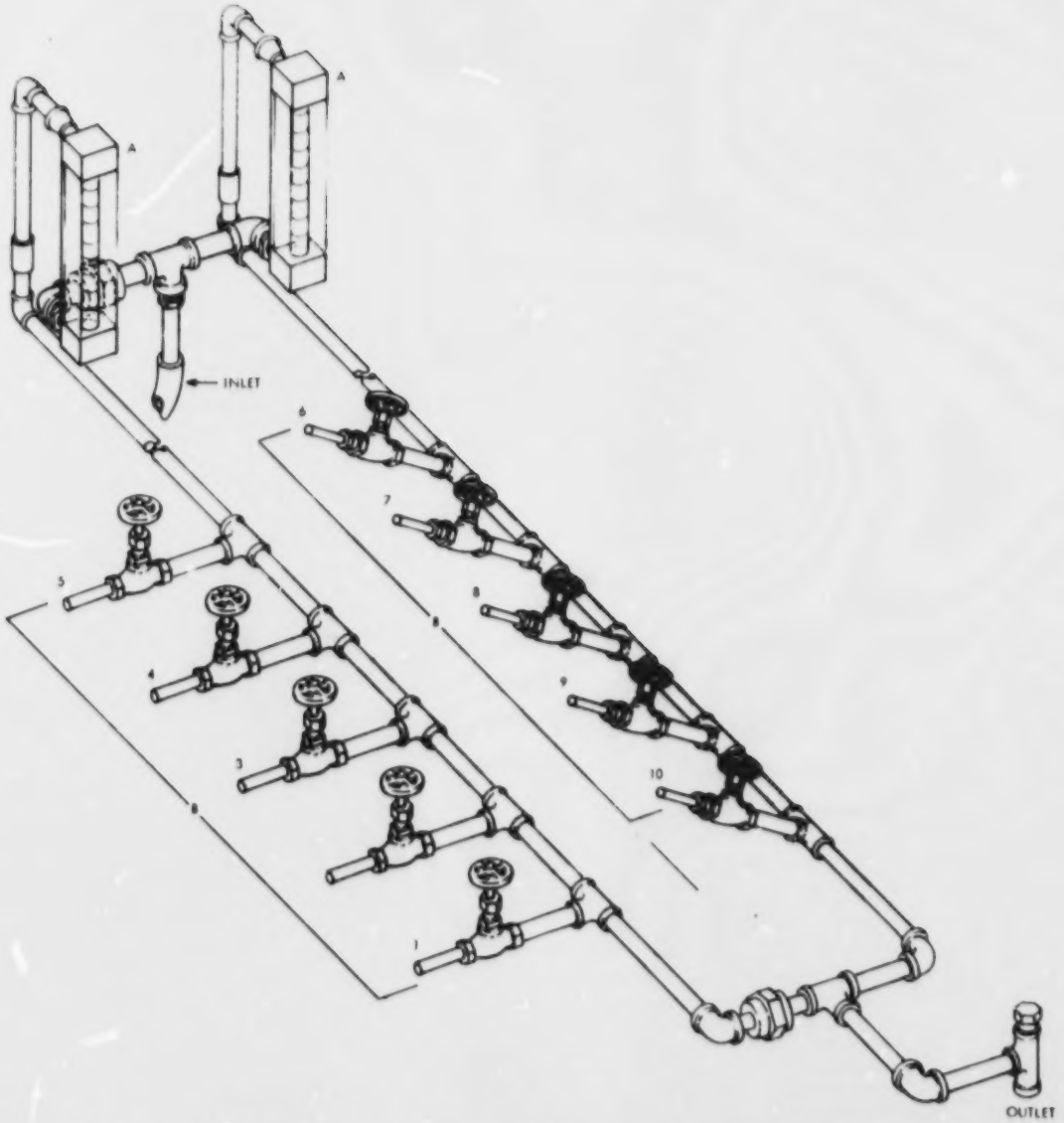
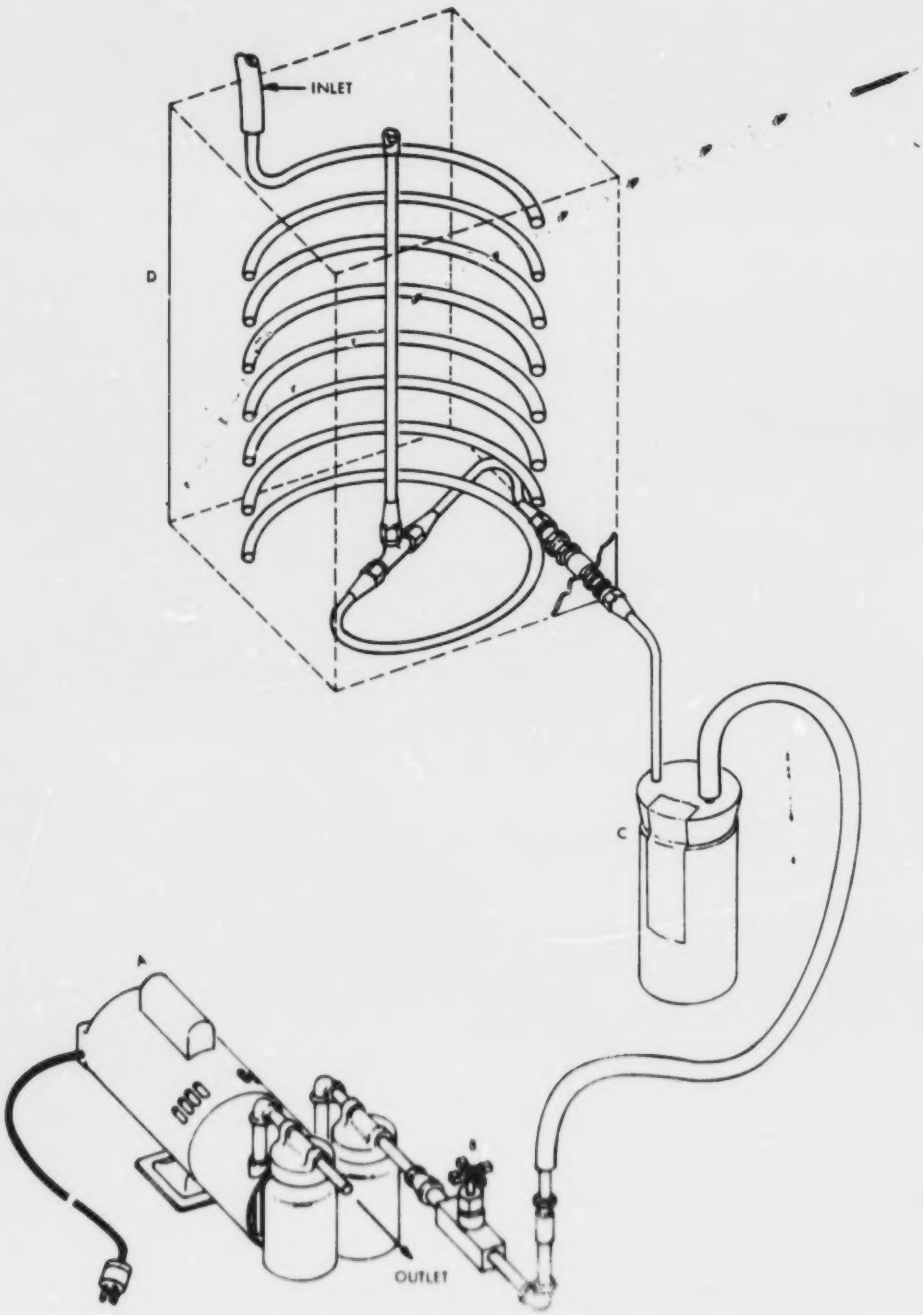


Figure 4. Drawing of sampling manifold, Fisher and Porter type FP-1/4-40-G-6 rotameters (A) were used to monitor the flowrate in each branch of the manifold. Sampling ports (B) were standard plumbing fittings with 1/4-in. pipe nipples attached.



Legend: The pump (A) is a GAST Model 0822-103-G27/X carbon vane pump with a capacity of 7 ft^3/min. Control valve (B) regulated sample flowrate. Water receiver (C) is a 32-oz jar and water condenser (D) is a galvanized box with a 1/2-in. copper tubing coil inside.

Figure 5. Pump and water condenser

Legend: Filter (A) is a polyethylene tube 1 in. in diameter and 3 ft in length. Rubber stoppers are used at each end and tube is packed 50/50 with silica gel and then with Ascarite. Filter is then connected to micrometer valve on inlet of Thomas diaphragm pump (B). Sample then goes to Matheson No. 602 rotameter (C), a Millipore filter (D) and then into Beckman No. 215A CO Analyzer (E). Bausch and Lomb VOM-5 Recorder (F) is used for readout. For calibration, gases were run into micrometer valve on pump.

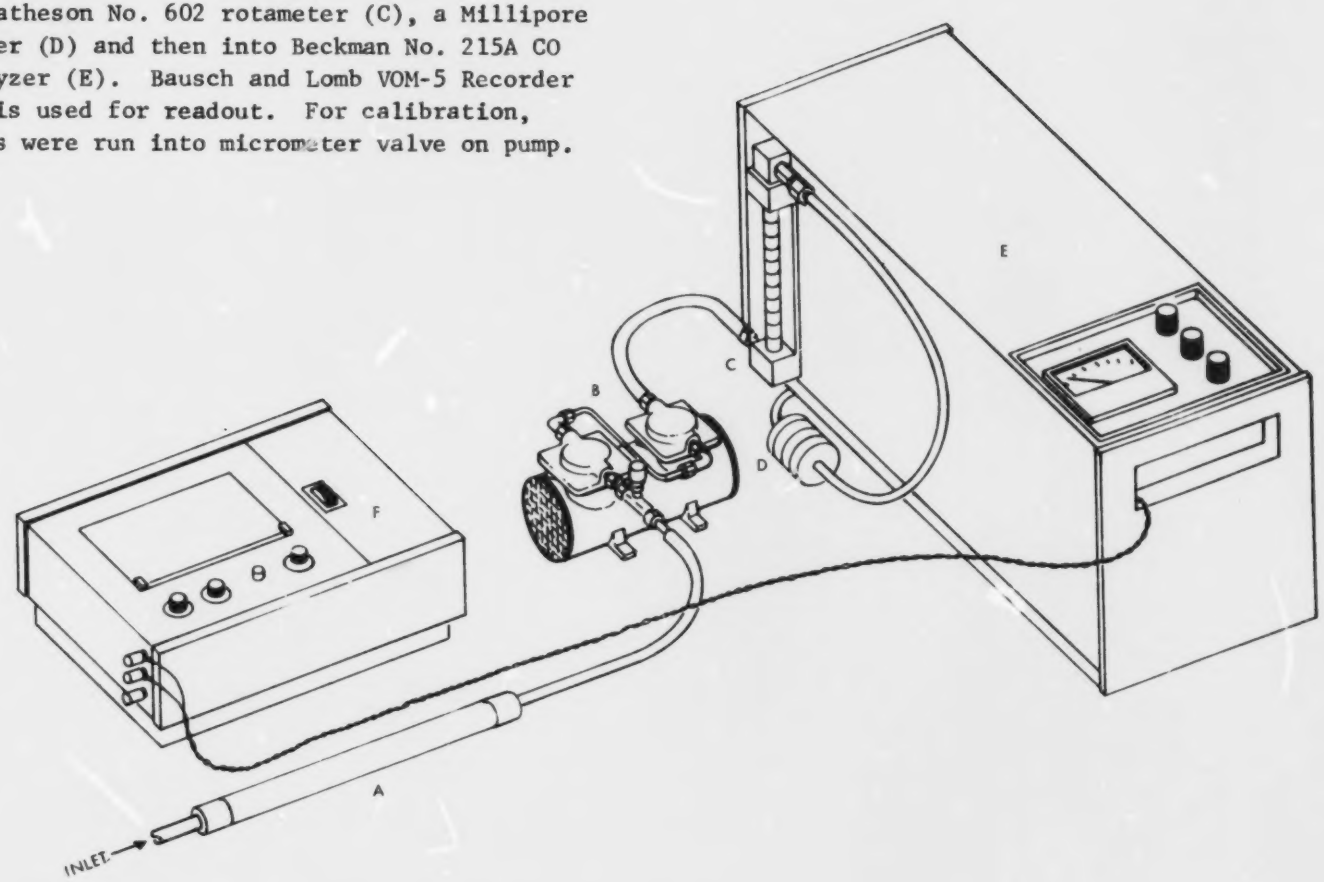


Figure 6. Continuous CO monitor

With the NDIR connected to a crude version of the manifold, the plant operators began reducing the excess air to the CO boiler until the CO level reached 500 ppm. This required a large deviation from normal operating conditions, but was attained and varied ± 100 ppm over a 1-hr period.

MRI personnel returned to the site in April with the manifold assembly completed for more complete testing of the system. After the manifold was connected the downpipe from the stack was found to be plugged. The pipe was cleared by pressurizing to about 30 psig briefly. At the full rated flow rate of 100 liters/min the manifold vacuum was about 250 mm Hg but the vacuum decreased to less than 80 mm at 80 liters/min total flow. After the CO level had been stabilized at about 500 ppm a run was made for about 45 min. At that time the manifold pump stalled due to water in the pump chamber.

The recorder chart from this run is shown in Figure 7. From the weight changes of the filter traps, water was 5.0% and CO_2 was 9.1% in the gas stream. The average CO concentration was 452 ppm uncorrected and 412 ppm corrected for CO_2 content.

To protect the manifold pump from water condensate, the water condenser shown in Figure 5 was built upon returning to MRI. When the bath is filled with ice water, the gas at the exit from the trap is cooled to below ambient and all components downstream remain dry. The trap collected 200 to 300 ml of water per hour during operation.

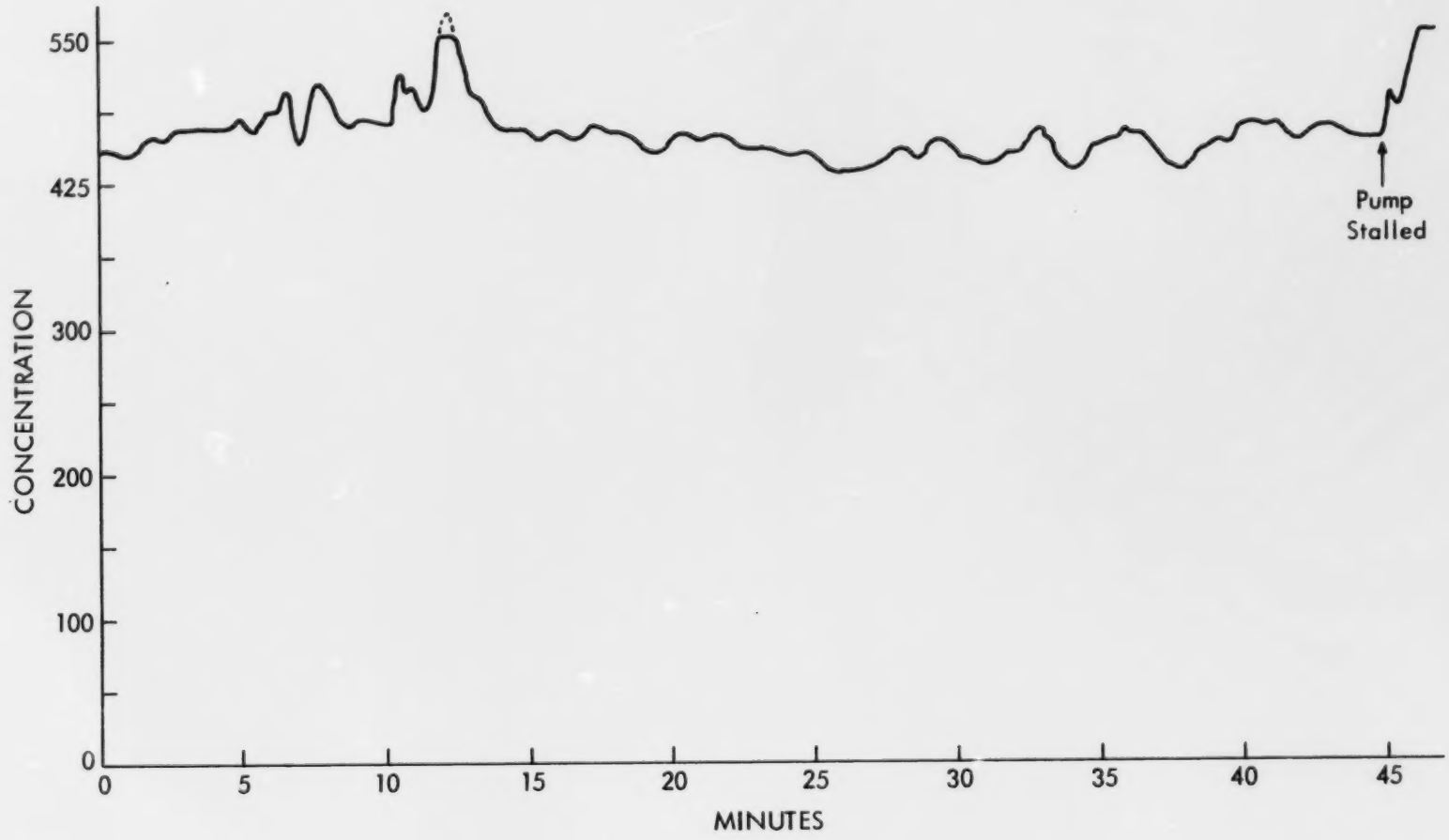


Figure 7. Results of preliminary test of Method 10

SECTION IV

EXPERIMENTAL DESIGN

GENERAL CONSIDERATIONS

Major considerations that entered into the experimental design of the collaborative test are summarized below.

1. Analysis Method - All collaborators would be instructed to follow the integrated sampling method of Method 10 as it appears in the 8 March 1974 edition of the Federal Register. Any deviations from the method by the collaborators would be noted by the MRI test supervisor.

2. Test Levels of CO - Two levels of CO are required. One level is near the proposed standard limit value--500 ppm. The second level is approximately half the concentration of the standard.

3. True Values of CO (determination of bias) - A set of six cylinders of CO in nitrogen from the National Bureau of Standards (NBS) would be sampled by the collaborators in the field. The CO concentrations of these cylinders ranged from 200 to 900 ppm and were accurate to < 1%. The collaborators were to analyze each cylinder three times. Three cylinders were to be analyzed on the first day of testing and the other three on the last day of the field test.

Since the test is designed to measure real samples at a refinery, and since the CO levels from the stack are not constant, a true value cannot be assigned to each run from the sampling manifold. MRI did have an NDIR continuously sampling the manifold concentration. The readings from this instrument were used primarily to monitor the CO levels during each test to ensure that the average CO level would be within the proper range. The values obtained from this instrument cannot be assumed to be any more accurate than any of the collaborators' instruments.

4. Sampling Time - Method 10 states that the sampling time shall be 1 hr.

5. Test Schedule - To obtain sufficient data for statistical analysis a total of 16 runs were made at each level. Four runs were made each day. Thus, the field sampling was arranged for two 5-day weeks of testing. The first day of testing was for setup and analysis of three of the NBS-certified cylinders and the last day for cleanup and analysis of the remaining NBS cylinders.

6. Number of Collaborators - The sampling manifold was designed to accommodate a maximum of 10 collaborators. Seven collaborators were deemed sufficient to obtain a cross section of the organizations involved with CO sampling, be within acceptable project costs, and provide sufficient data for the statistical analysis.

7. Interferences - Due to its low reactivity, carbon monoxide can be handled with most common materials of construction--glass, metals, plastic or rubber tubing. Water and carbon dioxide are known interferences in the NDIR analysis and these compounds are removed prior to introduction into the instrument. The method also measures the CO_2 content of the sample stream and corrects the NDIR concentration to that in the stack before CO_2 removal.

FORMAL DESIGN

The basic experimental model is:

$$X_{ijkl} = \mu + C_i + B_j + CB_{ij} + L_{k(j)} + LC_{ik(j)} + e_{l(ijk)} \quad ,$$

where

C_i = i^{th} collaborator, i = 1, . . ., 7;

B_j = j^{th} block of CO, j = 1, 2;

CB_{ij} = collaborator - block interaction;

$L_{k(j)}$ = k^{th} level nested within j^{th} block, k = 1, . . ., 16 for every j;

$LC_{ik(j)}$ = collaborator - level interaction;

μ = overall mean;

$e_{l(ijk)}$ = measurement error in the ijk^{th} cell, l = 1 for every ijk (not retrievable);

X_{ijkl} = $ijkl^{th}$ reading of CO (ppm).

Block* is considered a fixed factor (since we select the values of block), while collaborators and levels are considered to be random factors.

The expected mean squares are shown in Table 1.

Since a collaborator never measures the same CO concentration more than once, there is no direct estimate of σ_e^2 , i.e., no direct measure of the repeatability within collaborators. Thus, the sum $\sigma_e^2 + \sigma_{LC}^2$ is usually the denominator of an F-test, and the analysis of variance does not partition the sum into σ_e^2 and σ_{LC}^2 .

The potential existence of a genuine LC interaction is checked indirectly, however, via the Kendall concordance (W) method.** If no LC interaction exists, then the order of the collaborators should remain approximately stable during all runs; that is, the ranking of the collaborators should be nearly preserved from run to run. The Kendall W Method provides a quantitative measure of the agreement between runs and is used to give insight about the existence of LC interaction.

Thus, the analysis consists basically of the analysis of variance of the model, producing F-tests for C, B, CB and L effects, and estimates of the components of variance σ_e^2 , σ_C^2 , σ_{CB}^2 , etc., with a subsidiary check on the existence of an LC interaction (via Kendall W).

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* Originally, the readings within a block were to be considered replicates. However, examination of the data showed that the blocks could not be physically maintained constant, so "levels" were added to the model.

** Siegel, Sidney, Nonparametric Statistics, McGraw Hill, Inc., 1956, pp. 229-238.

Table 1. EXPECTED MEAN SQUARES (WHOLE EXPERIMENT)

Source	df	EMS
C	6	$\sigma_e^2 + 32\ \sigma_c^2 + \sigma_{LC}^2$
B	1	$\sigma_e^2 + 112\ \sigma_B^2 + 16\ \sigma_{CB}^2 + 7\ \sigma_L^2 + \sigma_{LC}^2$
CB	6	$\sigma_e^2 + 16\ \sigma_{CB}^2 + \sigma_{LC}^2$
L	30	$\sigma_e^2 + 7\ \sigma_L^2 + \sigma_{LC}^2$
LC	180	$\sigma_e^2 + \sigma_{LC}^2$
e	0	σ_e^2 (not retrievable)

SECTION V

FIELD TEST

MRI personnel arrived at the refinery site on 2 June 1974, to assemble the sampling manifold and prepare the site for the collaborative test which was to begin on the following day. The sampling system was assembled as shown in Figure 8, and able to operate at a total maximum flow rate of > 100 liters/min.

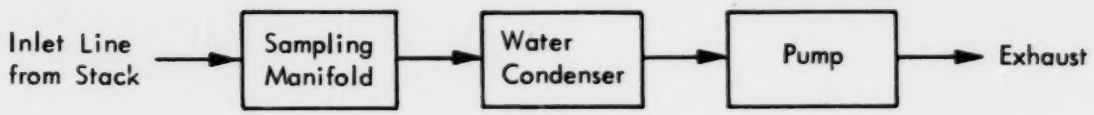

Figure 8. Block diagram of initial sampling manifold

On 3 June 1974, the collaborative test began with an orientation meeting at 0800. At the meeting each collaborator received a copy of the collaborator instructions (see Appendix C). At the meeting all collaborators except one reported that all equipment had arrived and they were ready to test. One collaborator's equipment had been delayed in transit.

The collaborators then proceeded to the refinery test site and, except for the one without equipment, began setting up equipment to begin sampling the check gases supplied by the National Bureau of Standards. Each collaborator was to analyze three of the gases on 3 June and the other three gases on 14 June. The collaborators began setting up their equipment on tables supplied at the test site, except for

Collaborator No. 5* who had his own sampling van at the site with his equipment set up inside the van. As the sampling of the check gases proceeded, light intermittent rain began falling, and the collaborators moved their equipment under shelter. Since most of the instruments had to be kept plugged in round-the-clock for proper stability, the field sampling was finally modified as follows: The Tedlar bags for two tests were filled according to the method at the field site. Then the bags were taken for analysis to the motel where the instruments were kept in the rooms.** Collaborators 2 and 5 kept their instruments in the van parked at the test site. In this manner two samples were taken in the morning and analyzed during the lunch break. Then two more samples were taken in the afternoon and analyzed at the end of the day. To accomplish this, some of the collaborators had to borrow a second bag and sample box from MRI due to lack of equipment.

Figures 9 to 11 show the test site and photographs of the collaborators at work.

Run No. 1--the first sampling run from the CO-boiler emissions--at the A level (~ 250 ppm) began at 1018 on 4 June 1974. All seven collaborators were ready for the test. The date and time for each run is given in Table 2.

Due to water condensing out in the two rotameters of the manifold, all collaborators sampled at a constant 400-cc/min rate during Runs Nos. 1 and 2. Heavy rain during the afternoon of 4 June forced the postponement of Tests 3 and 4 until the following day. To eliminate the water condensation in the rotameters the ice-cooled condenser was moved to a point upstream from the rotameters as shown in Figure 12.

During the first three tests it became apparent that the cardboard drums--which most of the collaborators had--could not withstand the negative pressure of about 50 mm Hg at the sample ports with a flow rate of 20 liters/min through each branch of the manifold.

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* Hereafter the collaborators will be referred to by randomly assigned designations: Collaborator 1, Collaborator 2, etc.

** Since the refinery had no protected area of sufficient size where the collaborators' instruments could be set up for the duration of the test schedule, and there was inclement weather, this precautionary step was necessary.

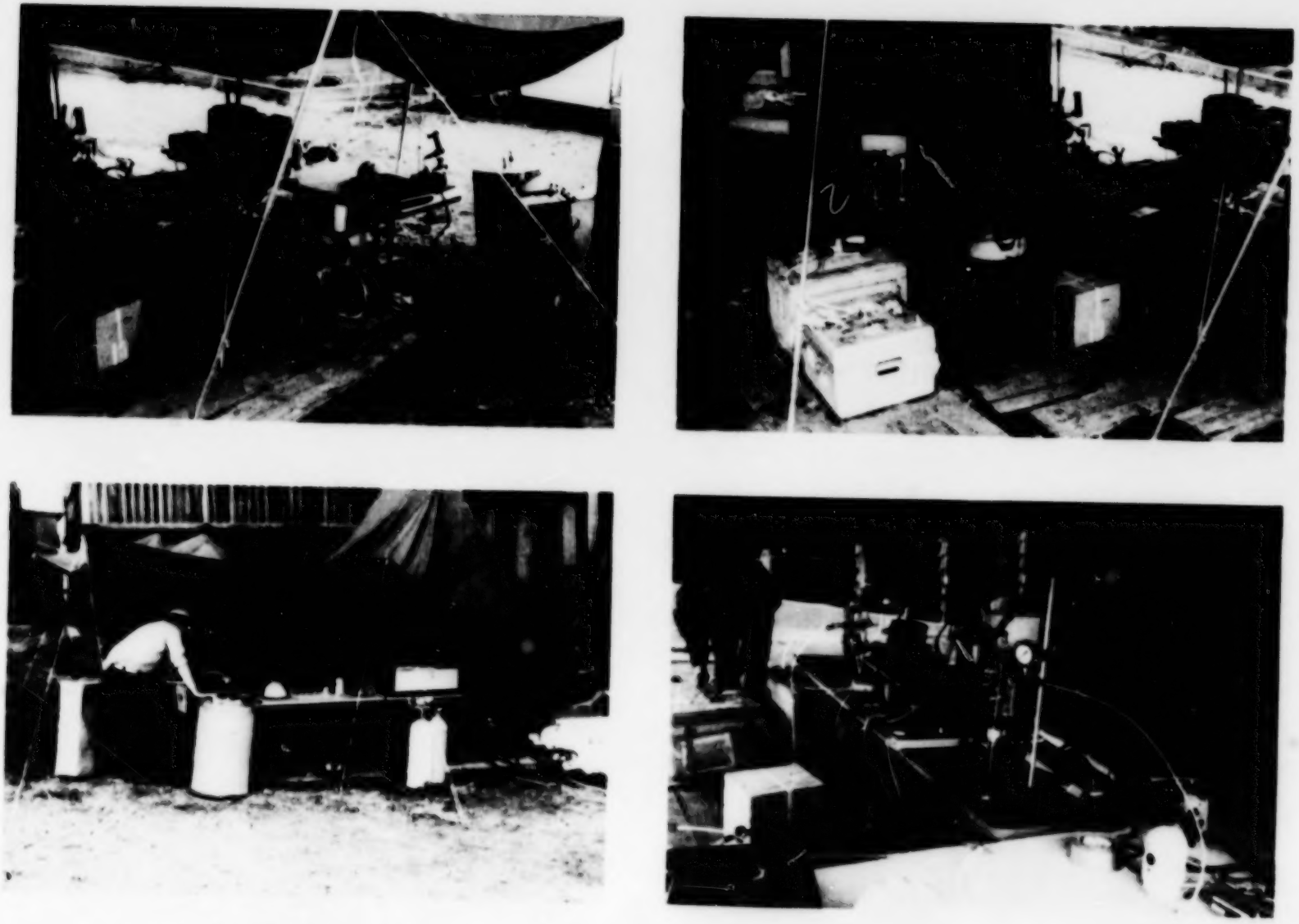
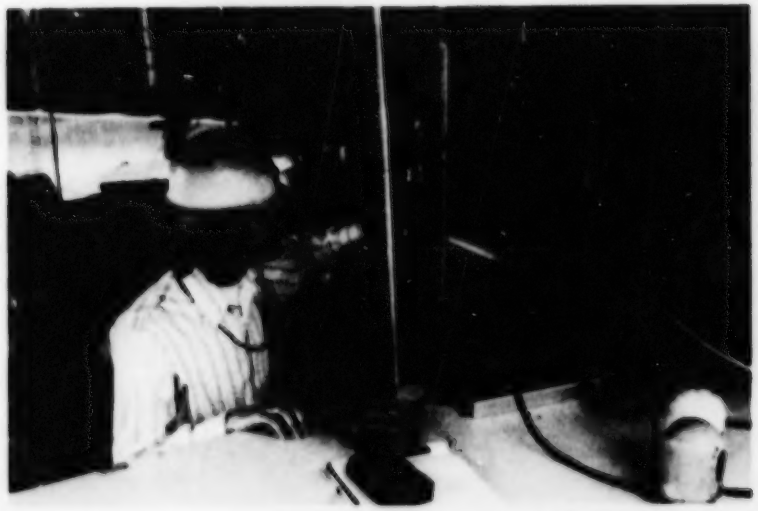
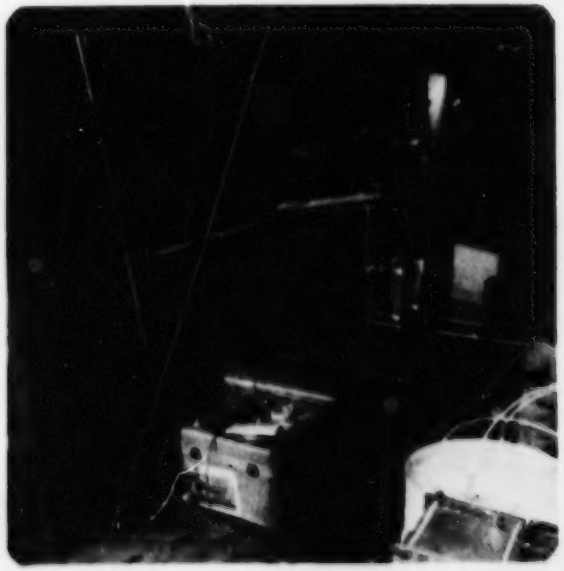


Figure 9. Photographs of the test site - CO collaborative test, El Dorado, Kansas



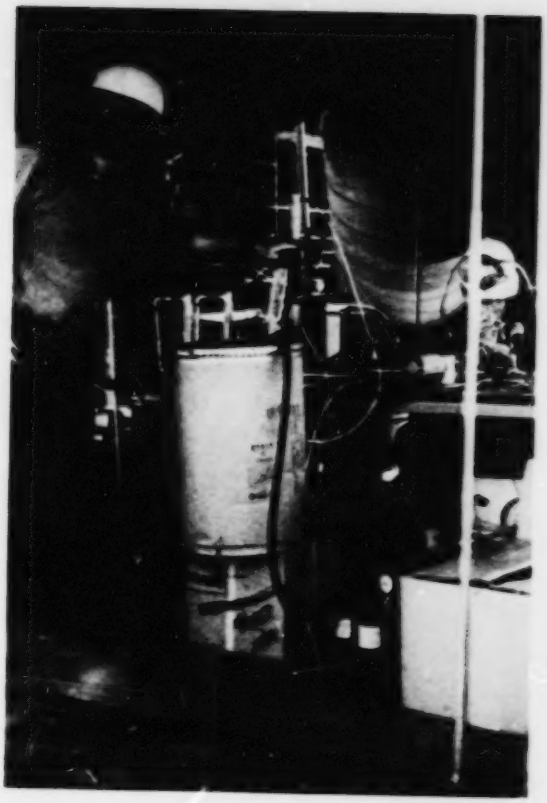
A. Roger Johnson (Interpoll)

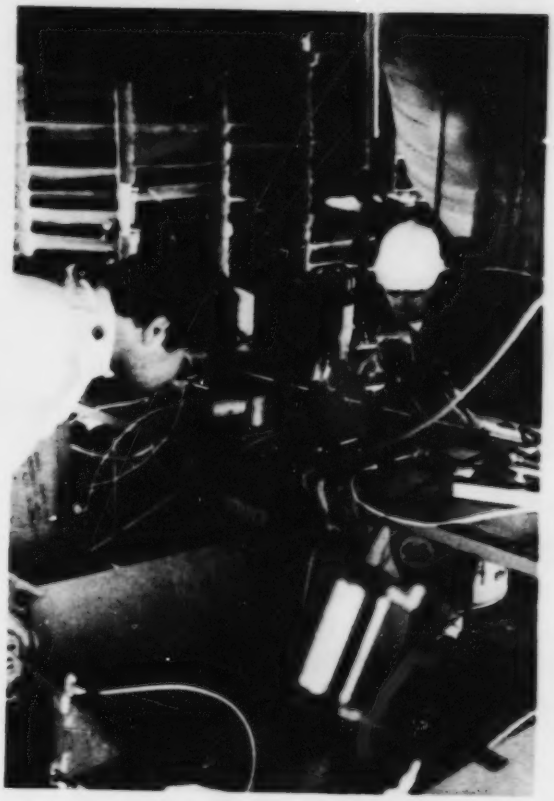
C. Maynard Johnson (Scott)



B. Mike Hartman (TRW)

Figure 10. Collaborators at work





A. Bill McClarence (Environmental Triple S)

B. Joe Schiappa (Entropy Environmentalists). Dan Briggs (Coors) in background

No photograph available of Sam Humphries (Ecology Audits)

Figure 11. Collaborators at work

Table 2. CO EMISSIONS SAMPLING SCHEDULE

Run no.	Date	Start	Stop	Comments
1A	6/4/74	1018	1118	Sampling flow constant at 400 cm^3/min.
2A	6/4/74	1146	1246	Sampling flow constant at 400 cm^3/min.
3A	6/5/74	0939	1039	Approximately 400 cm^3/min sampling rates proportional to total flow, H_2O condenser now ahead of manifold.
4A	6/5/74	1139	1239	Pump now between condenser and manifold.
5A	6/5/74	1458	1558	Manifold flowrate decreasing during run.
6A	6/5/74	1616	1716	Cloudy--no rain.
7A	6/6/74	0851	0951	Manifold flowrate still decreasing.
8A	6/6/74	1005	1105	Manifold flowrate still decreasing.
9A	6/6/74	1315	1415	Change to ~ 600 cm^3/min proportional sampling.
10A	6/6/74	1430	1530	Manifold flowrate now stable.
11A	6/7/74	0856	0956	Variable weather conditions 6/5-7.
12A	6/7/74	1015	1115	Little rainfall.
13A	6/7/74	1336	1436	
14A	6/7/74	1450	1550	
15A	6/14/74	0840	0940	
16A	6/14/74	0957	1057	
1B	6/10/74	0903	1003	Fair weather during second week of test.
2B	6/10/74	1019	1119	
3B	6/10/74	1327	1427	
4B	6/10/74	1448	1548	
5B	6/11/74	0906	1006	Power loss after first attempt to start run.
6B	6/11/74	1024	1124	
7B	6/11/74	1317	1417	
8B	6/11/74	1436	1536	
9B	6/12/74	0848	0948	Run deleted - CO concentration too high.
10B	6/12/74	1010	1110	
11B	6/12/74	1133	1233	
12B	6/12/74	1439	1539	
13B	6/12/74	1552	1652	
14B	6/13/74	0842	0942	
15B	6/13/74	1002	1102	
16B	6/13/74	1256	1356	
17B	6/13/74	1411	1511	

Figure 12. Block diagram of sampling manifold used for Test 3A

The collaborators also had difficulty maintaining air-tight systems under these conditions. Any leaks that appeared in one collaborator's sampling lines would then allow ambient air to enter the manifold and affect other collaborators' results as well. To alleviate the problem, the manifold system pump was moved to a point upstream of the manifold as shown in Figure 13. This change was carried out before starting Run 4A. All runs from this point onward used this manifold system with a slight positive pressure maintained at the sampling ports.

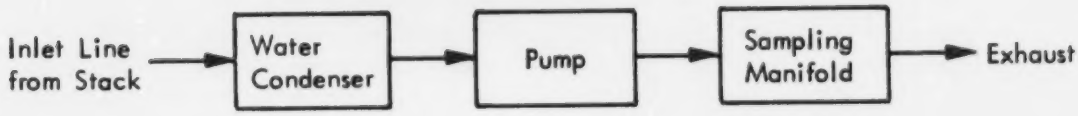


Figure 13. Block diagram of sampling manifold used for all tests after 3A.

The condenser protected the pump from water and the carbon vane centrifugal pump was well sealed and contained no oil or other substances which might contaminate the sample stream. Thus, the sampling ports of the manifold could be maintained at positive pressure without causing any bias in the results or unreliability of the sampling system components. All collaborators could then sample a uniform gas stream with no possibility that a leak or other malfunction in one collaborator's system could affect anyone else's results.

By the end of the day of 6 June, the high winds and heavy rains which hampered operations earlier in the week ended. During the weekend of 8 to 9 June, very high winds and heavy rains overturned the tables supporting the manifold but caused only minor damage to the equipment which did not delay testing. Hot, fair weather existed throughout the second week of the test.

As the first sets of preliminary results were reported in the field to MRI's test supervisor, potentially serious errors appeared in the results of the CO_2 analysis by the Ascarite weighing method. The weight changes of the Ascarite traps were varying widely. The weight of the impinger with its charge of Ascarite was simply too great compared to the slight change in weight due to the CO_2 absorbed.

Furthermore, a serious design fault in the Ascarite impinger system also appeared. As the glass inlet tube was inserted into the bed of Ascarite in the impinger, it became plugged with Ascarite. Carbon dioxide from the sample gas then converted the Ascarite in and around the end of the glass tube to a rock-hard plug after a period of time which varied from a few minutes to about 2 hr of operation. The interruptions in the gas flow could be alleviated by one of two methods. If a long, flexible tube packed with Ascarite was used instead of the impinger, solid plugs did not form if the tube had an I.D. of $\geq$ 25 mm. Instead, the Ascarite was progressively exhausted along its length. The second method of preventing Ascarite fouling was to place the silica gel and Ascarite as separate layers in a single impinger. With the Ascarite layer above the silica gel the glass tube could penetrate the bed without plugging and the gas stream then contacted the Ascarite over an area sufficient to prevent flow interruption.

By the beginning of the second week of testing, all collaborators had adopted one of the two methods of CO_2 removal and no further problems were reported with plugged CO_2 traps. Also, all collaborators used only Orsat-type CO_2 analysis during the second week of testing after the decision was made, with the approval of the EPA project monitor, to abandon the Ascarite weighing method for CO_2 determination.

During the first 3 days of testing the sample stream flow rate repeatedly decreased by as much as 50% over the 1-hr period of a run. Tests made between runs showed no decrease in the maximum flow rate when the control valve was opened fully. However, a heavy buildup of rust and fly ash particles was found in the valve. By 7 June, the flow had stabilized and remained reasonably constant for all subsequent tests. The flow changes were probably caused by partial blockage of the control valve by the rust and fly ash which had accumulated in the pipe running down the stack during the period before the collaborative test began.

Beginning with Run 8A the collaborators were allowed to increase their proportioned sampling rate to $\sim$ 600 cm^3/min after it was determined that all collaborators had sufficiently large Tedlar bags to obtain a larger sample volume.

To regain the two runs lost due to rain on 4 June, the test schedule was modified slightly by having the collaborators sample the NBS check gases whenever they had time during the testing so that the morning of 14 June, the last scheduled day of testing, could be used to obtain two additional runs at the A level of CO for a total of 16 runs at each level. By 13 June, all collaborators had sampled and analyzed all six cylinders of check gases in triplicate.

Testing at level B (~ 500 ppm) was carried out during 10 to 13 June. Run 5B was started at 0848 on 11 June, but a power loss occurred 3 min after the test started on one of the circuits used for the test equipment.

The power failure was caused when refinery personnel accidentally tripped a circuit breaker. After power was restored, the run was restarted after all collaborators had reevacuated their sample bags.

During the first half of Run 9B the MRI CO monitor showed > 1,000 ppm CO. When the refinery control room personnel attempted to correct the CO boiler excess air, the CO boiler went briefly into a state of incomplete combustion. The control room instruments showed combustible gases in the CO boiler exhaust for about 2 min before the process was brought back under control. When Collaborator 5 analyzed his sample immediately after the end of the run, he reported the CO level was far above 1,000 ppm. The collaborators were then instructed to delete Sample 9B and, if necessary, pump out the sample bag for that run so that two samples could still be taken before breaking for lunch.

Runs 15A and 16A were made on the morning of 14 June. All equipment was then dismantled and the site cleaned. After a final meeting the site was vacated by 1500 on 14 June.

SECTION VI

RESULTS OF ANALYSES

This section discusses the results which the collaborators submitted to MRI after the field test. Significant variations from Method 10 are also noted. The last part of this section contains the measurements obtained by the MRI monitoring device. Results from collaborators are contained in Volume II of this report.

COLLABORATORS' RESULTS

A summary of the results which the collaborators submitted to MRI is shown in Tables 3 to 5 and Figures 14 to 16. Table 3 and Figure 14 show results for Level A (200 to 300 ppm) and Table 4 and Figure 15 show results for Level B (400 to 600 ppm). The two sets of data overlap on some runs due to the difficulty in maintaining a constant level. Table 5 and Figure 16 show the collaborators' results from their analyses of the NBS-certified standard gases, and the values MRI obtained from reading the collaborators' recorder charts.

The large errors found in Collaborator 7's results for the NBS standard gases were traced to inaccurate span gases. The consistently high results on the NBS gases were noted during the test. In an effort to identify the cause, another collaborator's span gases were analyzed on Collaborator 7's instrument. Using the other collaborator's span gases, the NBS gas results agreed with the predicted values. From the NBS gas data, the span gases used by Collaborator 7 were approximately 30% higher than the certified value. Since such an error would not have been detectable if all collaborators were operating independently, Collaborator 7 could make no correction in his results.

Table 3. COLLABORATORS' RESULTS FOR LEVEL A (200-300 ppm CO)

		Run Number															
		1A[a]	2A[a]	3A[a]	4A	5A	6A	7A	8A	9A	10A	11A	12A	13A	14A	15A	16A
(1)[b]	Instrument reading (ppm CO)	235	885	640	330	300	350	295	263	298	355	325	290	295	305	295	270
	MRI readings[c]	(245)	(885)	(650)	(335)	(305)	(350)	(320)	(270)	(305)	(363)	(335)	(290)	(300)	(310)	(295)	(275)
	Percent CO_2 measured	12.2	15.5	14.0	15.0	13.5	15.5	13.5	13.5	13.0	15.0	14.5	13.0	14.0	14.0	15.0	14.0
	Stack CO level (ppm)	207	748	550	281	260	296	255	228	259	302	278	252	254	262	251	232
(2)	Instrument reading (ppm CO)	342	324	540	295	302	345	345	280	335	365	310	330	325	315	335	341
	MRI readings[c]	(346)	(328)	(541)	(297)	(298)	(350)	(342)	(257)	(333)	(367)	(307)	(333)	(324)	(315)	(333)	(341)
	Percent CO_2 measured	13.6	9.0	12.2	12.7	12.2	12.5	13.5	12.5	13.6	12.3	13.7	13.2	14.4	13.6	14.6	15.2
	Stack CO level (ppm)	295	295	474	258	265	302	298	245	289	320	268	286	278	272	286	289
(3)	Instrument reading (ppm CO)	335	418	-	325	300	330	340	290	357	370	290	323	310	318	309	313
	MRI readings[c]	(323)	(404)	-	(335)	(305)	(335)	(332)	(292)	(359)	(374)	(285)	(320)	(304)	(314)	(294)	(304)
	Percent CO_2 measured	Neg.	Neg.	-	12.6	13.2	13.9	14.9	14.2	14.2	14.8	14.2	15.1	13.0	13.5	15.1	15.0
	Stack CO level (ppm)	-	-	-	284	260	284	283	249	307	315	249	284	270	275	262	266
(4)	Instrument reading (ppm CO)	71	212	247	286	249	291	244	210	177	204	194	207	125	119	308	332
	MRI readings[c]	(53)	(216)	(251)	(289)	(260)	(296)	(251)	(212)	(184)	(210)	(198)	(213)	(129)	(123)	(314)	(333)
	Percent CO_2 measured	2.8[d]	8.4[d]	5.1[d]	14.0[d]	12.7[d]	12.9[d]	7.5[d]	4.5[d]	7.2[d]	8.8[d]	8.3[d]	10.6[d]	6.2[d]	6.8[d]	13.7	14.8
	Stack CO level (ppm)	69	194	234	246	228	253	226	181	164	186	178	185	117	111	266	283
(5)	Instrument reading (ppm CO)	416	406	-	273	272	311	315	257	281	315	270	280	286	283	300	300
	MRI readings[c]	(415)	(405)	-	(273)	(270)	(315)	(315)	(255)	(285)	(315)	(270)	(280)	(285)	(285)	(300)	(300)
	Percent CO_2 measured	13.6[d]	6.8[d]	-	14.3[d]	14.3[d]	20.5[d]	15.8[d]	5.9[d]	12.5[d]	7.0[d]	12.0[d]	0	7.6[d]	13.7[d]	14.4	14.9
	Stack CO level (ppm)	359	378	-	234	233	247	265	242	246	293	238	280	264	244	257	253
(6)	Instrument reading (ppm CO)	380	379	820	319	280	319	300	250	295	320	265	285	260	266	250	256
	MRI readings[c]	(380)	(379)	(820)	(319)	(280)	(319)	(300)	(250)	(295)	(320)	(265)	(285)	(260)	(266)	(250)	(275)
	Percent CO_2 measured	16.0	16.2	15.4	13.6	13.0	14.2	14.6	14.8	14.5	14.7	14.7	15.2	14.6	14.4	14.1	14.7
	Stack CO level (ppm)	319	318	694	276	244	274	256	213	252	273	226	242	222	227	215	218
(7)	Instrument reading (ppm CO)	430	430	1,184	320	-	-	370	240	350	400	40	50	450	290	340	360
	MRI readings[c]	(448)	(456)	(1,185)	(380)	-	-	(390)	(253)	(380)	(428)	(40)	(50)	(472)	(305)	(355)	(400)
	Percent CO_2 measured	26.3[d]	29.1[d]	5[d]	[illegible][d]	-	-	0.6[d]	0.6[d]	0.6[d]	0.6[d]	0[d]	0[d]	12.4[d]	8.7[d]	14.0	15.0
	Stack CO level (ppm)	317	305	1,125	31[illegible]	-	-	347	225	328	375	40	50	394	265	292	306

a/ These runs were made under negative pressure.
b/ Collaborator.
c/ Readings MRI obtained from collaborators' recorder charts.
d/ Value obtained by Ascarite weight gain.

Table 4. COLLABORATORS' RESULTS FOR LEVEL B (400-600 ppm CO)

		Run Number														
		1B	2B	3B	4B	5B	6B	7B	8B	10B[a]	11B	12B	13B	14B	15B	16B	17B
(1)[b]	Instrument reading (ppm CO)	400	170	450	460	495	420	435	510	745	655	492	390	576	390	515	580
	MRI readings[c]	(405)	(175)	(460)	(470)	(500)	(420)	(440)	(510)	(745)	(665)	(490)	(400)	(580)	(395)	(530)	(590)
	Percent CO_2 measured	14.0	7.0	14.0	14.0	15.0	14.0	15.0	15.0	14.0	14.0	15.0	14.0	15.0	14.0	13.0	14.0
	Stack CO level (ppm)	344	158	387	396	421	361	370	434	461	563	418	335	490	335	448	499
(2)	Instrument reading (ppm CO)	425	425	510	615	495	470	450	580	770	640	535	400	550	445	640	650
	MRI readings[c]	(427)	(422)	(505)	(617)	(496)	(475)	(453)	(582)	(737)	(643)	(490)	(495)	(548)	(445)	(639)	(648)
	Percent CO_2 measured	13.6	12.5	14.4	14.4	13.6	15.2	15.4	15.6	14.1	14.8	14.2	14.6	13.2	15.2	14.7	14.9
	Stack CO level (ppm)	367	372	437	526	428	399	381	490	661	545	459	342	477	377	546	553
(3)	Instrument reading (ppm CO)	430	365	545	600	538	455	443	565	745	695	505	440	611	428	625	635
	MRI readings[c]	(420)	(355)	(535)	(600)	(535)	(450)	(437)	(561)	(742)	(692)	(505)	(440)	(609)	(418)	(629)	(624)
	Percent CO_2 measured	13.0	13.5	13.5	14.0	14.4	13.8	14.5	14.2	14.0	14.0	13.5	13.5	14.2	15.2	13.7	13.5
	Stack CO level (ppm)	374	316	471	516	461	391	379	485	641	598	437	381	524	363	539	545
(4)	Instrument reading (ppm CO)	307	293	456	474	455	404	447	546	515	513	498	256	596	424	647	629
	MRI readings[c]	(313)	(279)	(475)	(484)	(464)	(443)	(454)	(554)	(541)	(540)	(507)	(265)	(605)	(435)	(663)	(642)
	Percent CO_2 measured	13.1	13.5	12.4	7.8	13.6	12.8	12.1	10.6	13.8	13.8	13.6	7.6	13.8	13.2	13.7	12.4
	Stack CO level (ppm)	267	248	399	437	393	352	393	488	444	442	430	241	514	368	588	551
(5)	Instrument reading (ppm CO)	372	362	478	526	441	397	410	510	660	606	445	408	540	385	603	594
	MRI readings[c]	(370)	(360)	(460)	(530)	(440)	(400)	(410)	(515)	(660)	(608)	(450)	(412)	(535)	(385)	(594)	(594)
	Percent CO_2 measured	13.6	12.0	13.6	13.4	14.3	14.4	15.0	14.6	14.1	14.8	15.0	14.4	14.0	14.6	14.9	14.9
	Stack CO level (ppm)	321	319	413	456	378	340	349	436	567	516	378	349	464	329	514	506
(6)	Instrument reading (ppm CO)	360	380	479	580	445	404	509	507	685	640	440	400	575	385	619	590
	MRI readings[c]	(360)	(380)	(479)	(580)	(445)	(404)	(509)	(507)	(685)	(640)	(440)	(400)	(575)	(385)	(619)	(590)
	Percent CO_2 measured	13.4	15.2	14.7	14.6	14.8	14.7	15.0	14.6	14.9	14.5	14.6	14.3	14.5	14.8	15.0	14.9
	Stack CO level (ppm)	312	322	409	495	379	345	434	431	583	547	376	343	492	328	523	504
(7)	Instrument reading (ppm CO)	360	330	620	780	610	540	540	710	-	840	580	520	710	510	830	840
	MRI readings[c]	(385)	(355)	(632)	(795)	(615)	(561)	(556)	(671)	-	(844)	(590)	(538)	(735)	(531)	(830)	(845)
	Percent CO_2 measured	13.5	13.5	14.1	14.0	14.6	14.5	14.5	14.2	-	13.6	13.5	13.0	13.8	14.0	13.1	14.0
	Stack CO level (ppm)	311	285	533	671	521	462	462	609	-	726	502	452	612	439	721	722

a/ Run No. 9B was deleted - CO level > 1,000 ppm.
b/ Collaborator
c/ Readings MRI obtained from collaborators' recorder charts.

Table 5. COLLABORATOR RESULTS OF NBS STANDARD GASES

		Gas cylinder no.											
		1 (517 ppm)		2 (734 ppm)		3 (903 ppm)		4 (480 ppm)		5 (258 ppm)		6 (239 ppm)	
		Reading	MRI's value[a]	Reading	MRI's value[a]	Reading	MRI's value[a]	Reading	MRI's value[a]	Reading	MRI's value[a]	Reading	MRI's value[a]
(1)[b]	Run 1	522	535	730	735	900	900	490	495	275	275	270	265
	2	522	535	734	740	900	900	490	495	275	275	270	260
	3	522	535	735	745	900	895	492	500	275	275	270	260
	Average	522		733		900		491		275		270	
(2)	Run 1	540	538	740	716	930	930	510	506	295	294	290	286
	2	540	538	750	738	920	920	520	513	300	298	280	281
	3	540	538	750	738	915	915	523	513	295	294	275	277
	Average	540		747		922		518		297		282	
(3)	Run 1	537	518	760	768	903	912	510	507	268	278	270	264
	2	537	518	760	768	902	911	510	507	267	278	270	264
	3	536	517	760	768	902	911	510	507	268	278	270	264
	Average	537		760		902		510		268		270	
(4)	Run 1	542	520	740	770	871	895	506	528	289	294	265	269
	2	542	520	756	770	875	895	508	528	285	290	265	271
	3	538	520	758	770	872	895	520	533	287	295	264	271
	Average	541		751		873		511		287		265	
(5)	Run 1	494	493	686	695	800	815	450	470	252	245	241	245
	2	489	490	695	700	790	800	464	465	251	245	245	245
	3	489	490	675	680	790	800	464	465	264	250	248	250
	Average	491		685		793		466		256		245	
(6)	Run 1	510	510	740	740	910	910	490	490	250	250	250	250
	2	510	510	745	745	910	910	485	485	250	250	245	245
	3	-	-	-	-	-	-	-	-	-	-	-	-
	Average	510		742		910		488		250		248	
(7)	Run 1	730	708	1,010	1,010	1,200	1,200	685	659	370	344	332	305
	2	730	708	1,015	1,015	1,200	1,200	685	659	370	339	332	305
	3	730	703	1,015	1,020	1,200	1,200	685	659	370	339	332	305
	Average	730		1,013		1,200		685		370		332	

[a] Readings MRI obtained from collaborators' recorder charts.
[b] Collaborator.

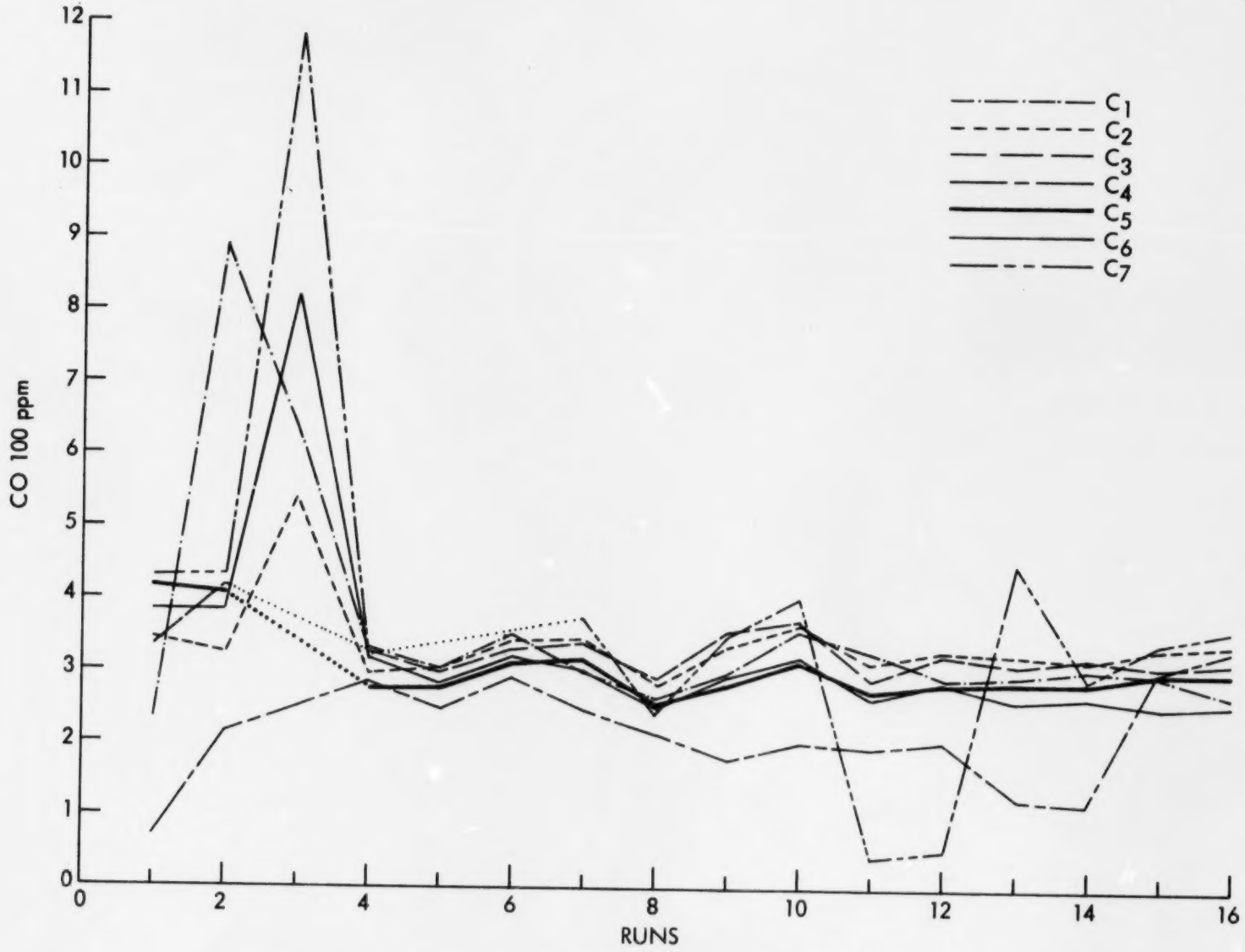


Figure 14. Collaborators' results for Block A (200-300 ppm CO)

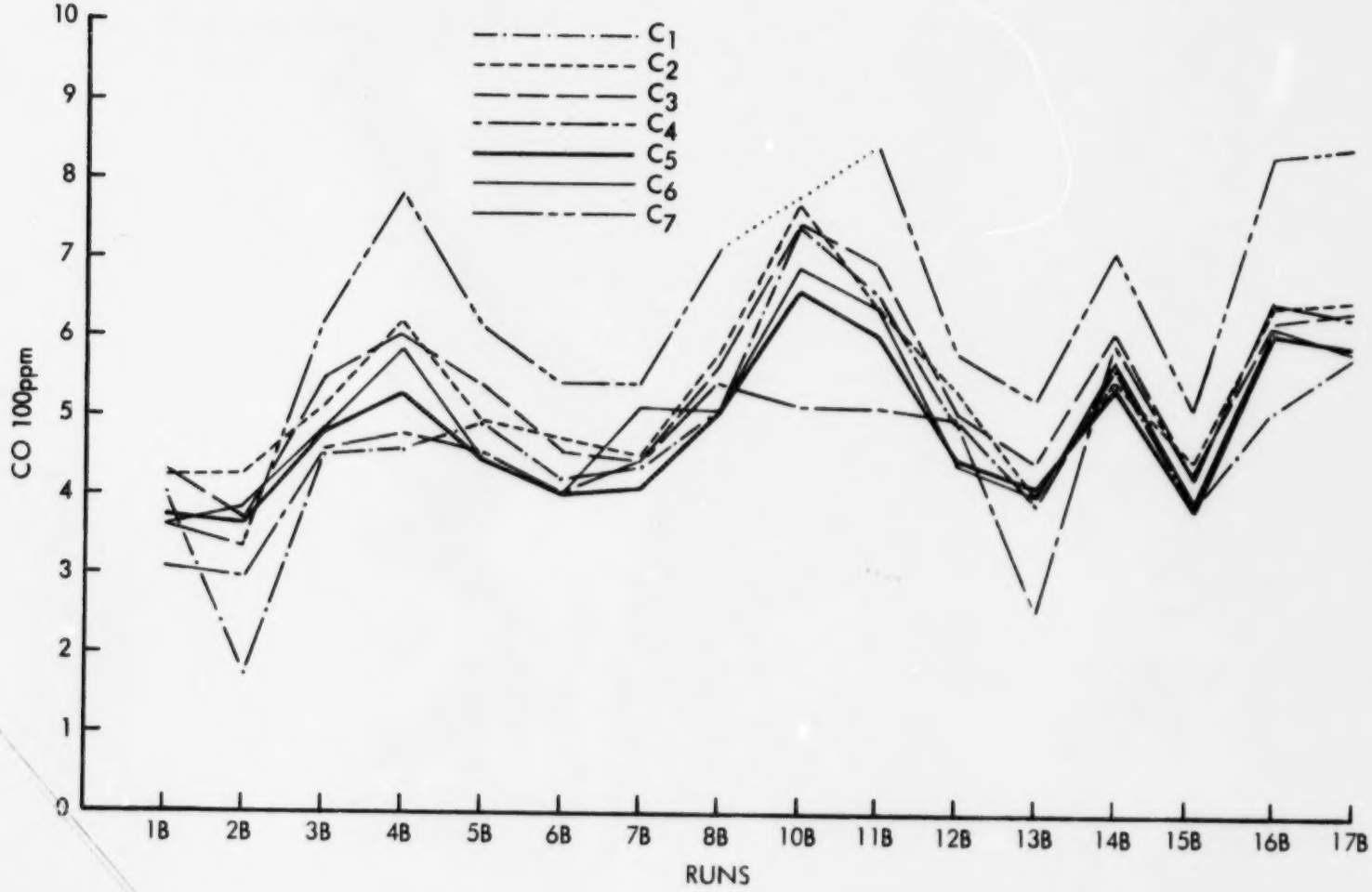


Figure 15. Collaborators' results for Block B (400-600 ppm CO)

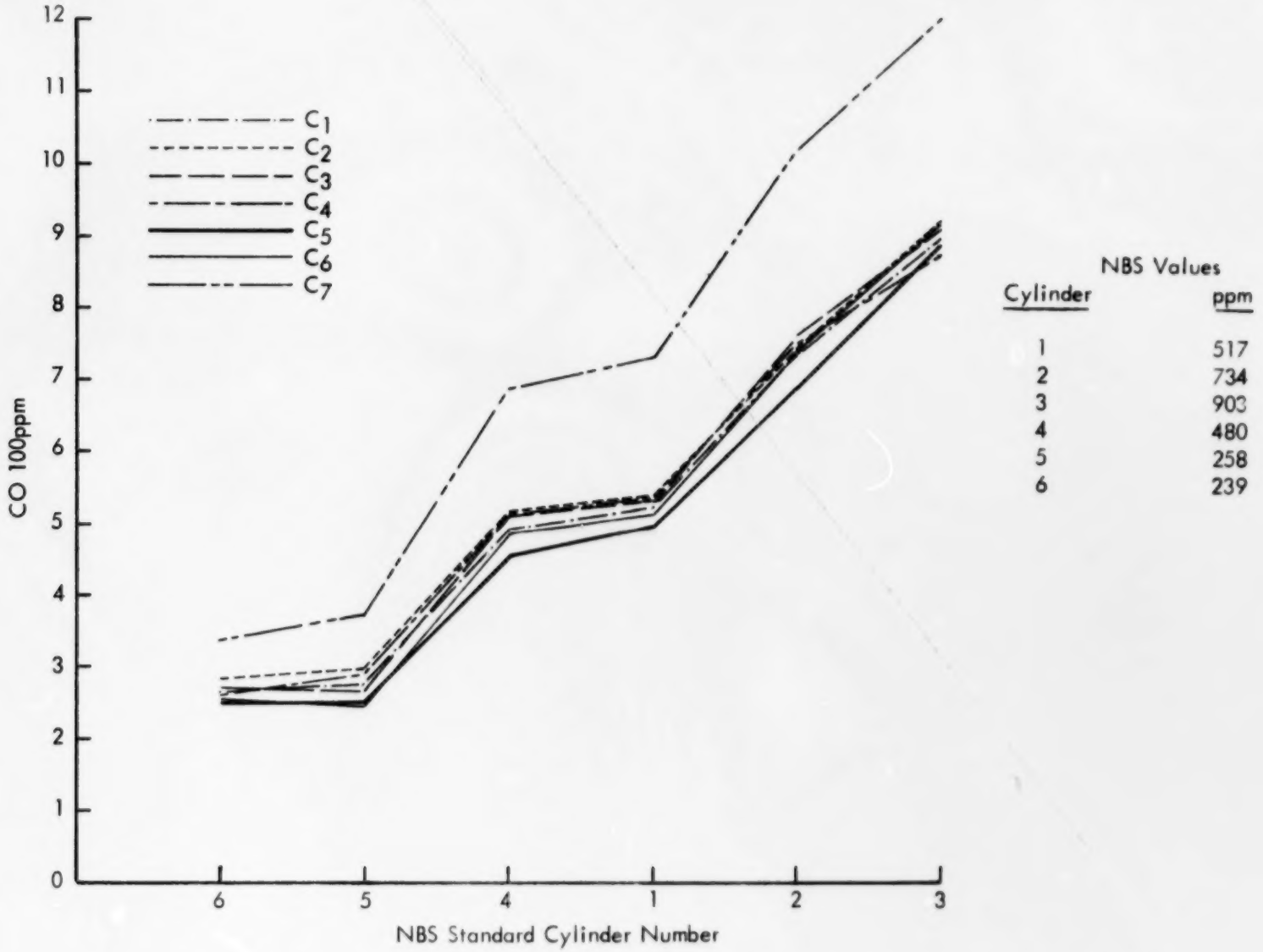


Figure 16. Collaborators' results of NBS standard gases

COLLABORATORS' INSTRUMENTATION AND DEVIATIONS FROM METHOD 10

The instrumentation used by each collaborator is noted. Deviations from Method 10 are also recorded. Comments with regard to the methods of calibrating and reading the instrument charts are based upon an analysis by MRI of the strip chart recordings which each collaborator supplied after completion of the field testing. Where the procedure used was unclear, MRI requested further information from the collaborator.

Collaborator No. 1 - Gas sample went from inlet to rotameter to water trap and then into a Universal Electric diaphragm pump. The pump forced a sample into a 3-ft^3 Tedlar bag. One bag was contained within its enclosure, which was a large cardboard shipping barrel. A second bag and enclosure was borrowed from MRI. The enclosure was a 1-ft x 3-ft x 4-ft aluminum case. Since the cardboard barrel leaked, a sample could not be pulled into bag as per Method 10. A Beckman 315A analyzer was used for analysis. The calibration gases used were supplied by Scott and certified as 807 ppm, 515 ppm, and 236 ppm CO. CO_2 was analyzed by the Fyrite analyzer. Impingers were used for CO_2 and H_2O removal traps.

Only high span (807 ppm CO) and zero gases were generally used before and after each run. Manufacturers' calibration data were used to correct nonlinearity.

Collaborator No. 2 - Sampling was done by Method 10. A 96-liter Saran bag enclosed in a 55-gal. steel drum was used by this collaborator. He borrowed a second bag from MRI--same construction as that borrowed by Collaborator 1. An MSA Lira 303 analyzer was used for CO analysis. Calibration gases of 591 ppm and 324 ppm CO supplied by Air Products were used. CO_2 was analyzed by Orsat. CO_2 and H_2O filters were clear plastic cartridges 5 cm in diameter and 10 cm long.

This collaborator did all analyses on-site in another collaborator's truck, ran both span gases and zero after each sample, and assumed a straight line between calibration points.

Collaborator No. 3 - Sampling was done by Method 10. This collaborator used 2.5 ft^3 Tedlar bags. One bag was used with a 2-ft x 3-ft x 2-ft fiberglass shipping case and the other was a similar rigid wooden packing case. An MSA Lira 200 CO Analyzer was used. Calibration gases used were supplied by Air Products and were certified as 258 ppm, 609 ppm and 965 ppm CO. Gas traps were made from 8-oz wide-mouth bottles. CO_2 was analyzed by the Fyrite analyzer.

A linear response was assumed. The 965- and 609-ppm standards were usually used with each set of two samples. Usually only the 965-ppm gas reading was used to determine results.

Collaborator No. 4 - After Run 3A, all sampling was done by Method 10. This collaborator used 1.5-ft^3 Tedlar bags in a 23-gal. cardboard drum. The analyses were done using an MSA Lira 300 Analyzer. Calibration gases used were supplied by Linde and were analyzed as 310 ppm, 520 ppm, and 690 ppm CO. Large impingers were used for CO_2 and H_2O filters, but finally a single impinger with separate beds of silica gel and Ascarite was used. A Fyrite Analyzer was used for CO_2.

Zero and 690-ppm gases were used with each sample. A linear response was assumed. The apparent CO concentration from a least-squares fit of calibration on five different days was used rather than the manufacturer-supplied value.

Collaborator No. 5 - Sampling was done by Method 10 with a 50-ft length of polyethylene tubing connected between the water condenser and the 36-liter Tedlar bag, which was enclosed in a Plexiglass case. A Beckman 315 AL CO Analyzer was used. Calibration gases were supplied by Liquid Air, analyzed at 827 ppm, 594 ppm, and 83 ppm CO. Large impingers were used initially for the CO_2 and H_2O traps. This was changed to a plastic bottle with a hole in the bottom for the exit tube after Test 14A. The Ascarite weighing method for CO_2 was used for the first 14 runs. The remaining runs were by Orsat.

This collaborator ran calibrations for each run and plotted a smooth curve through the points.

Collaborator No. 6 - Sampling was done by Method 10. One hundred-liter Tedlar bags were used with a 2-ft high cardboard drum. All bags for each day were analyzed together each evening. An Intertech Analyzer was used for CO analysis. Calibration gases were supplied by Matheson. Concentrations of 315, 660, and 1,050 ppm CO were used. An impinger was used for the silica gel and a length of plastic pipe for the Ascarite. An Orsat was used for CO_2 analysis.

This collaborator had the only CO analyzer with a linear response. The instrument had special linearizing circuits. Response was very linear over the entire range. All three standards were run once for each set of bags analyzed.

Collaborator No. 7 - Sampling was done by pumping the gas from the manifold into a 2-ft^3 Tedlar bag with a Universal Electric diaphragm pump. An MSA Lira 300 CO Analyzer was used. Calibration gases of 285, 600, and 1,000 ppm were supplied by Linde. A Fyrite Analyzer was used for CO_2. Testing began with separate small drying tubes for H_2O and CO_2 absorption. This was later changed to a single impinger with separate layers of silica gel and Ascarite. All three span gases were measured with each set of samples but only the zero and 1,000-ppm gases were used in calculating results. Samples were calculated using a manufacturer-supplied calibration curve but the standards were done by assuming a linear response.

General Comments - As can be seen from the preceding pages, the equipment and procedures used in Method 10 are far from being standardized at this time. A wide variety of sampling bags and enclosures were used by the collaborators. Due to the unexpected difficulty with the Ascarite, CO_2 traps, many different methods were used to alleviate the problem. Also, only one of the collaborators had a CO analyzer which had a linear output. The linearizing circuits increase the price of a CO analyzer significantly and have only recently been available from commercial sources. Thus most of the analyzers now in use will have a nonlinear output. However, many of the deviations from Method 10 had a small effect on the results of this collaborative test. While the Fyrite Analyzer is not capable of as high a precision as an Orsat Analyzer under controlled conditions, the Fyrite's simplicity and superior ruggedness make it more suitable for field work. The results by Orsat analysis were slightly more precise during this test but difference was small ($\sim$ 0.5%).

Most of the variations in sample bags, enclosures, and pumping arrangements would be expected to function as well as that specified by Method 10. Since the sampling lines must operate at ambient or slightly lower pressure, leaks are a severe problem in Method 10 and in the various modified methods used.

Some of the methods used in reading the recorder charts and calculating the CO levels leave much to be desired. Where the instrument output is nonlinear, a smooth curve drawn through several calibration points is probably the best method, although it is subject to errors in drawing the curved line. Use of a manufacturer-supplied curve can lead to trouble, since the shape of the curve does change with time. Assuming a straight-line relationship between calibration points can lead to very good or very bad results, depending on how far the sample reading is from the nearest calibration point.

A further problem was that the method does not state limits of accuracy for the rate meter used to monitor the sampling rate. The collaborators used a wide variety of meters for this function with accuracies of calibration and readability of from < 1% to ± 50%. Since the CO concentration of the gas stream did change very rapidly, imprecise control of sampling rate may have been a major contributor to the poor precision of the results.

MRI'S TEST RESULTS

The results from MRI's continuous monitor are given in Table 6. These results were obtained by assuming a linear response and measuring the areas under the curves which comprised the analog results of each run with a planimeter. The instrument's response is linear to about 400 ppm. Above this concentration response becomes increasingly nonlinear.

The results are in general agreement with those of the collaborators. No exact comparison is possible, however, because the analyzer went off scale frequently and because a leak was later discovered in the sampling pump which caused dilution of the sample gas to occur to some extent. Also the continuous method is simply a time average, while the integrated method is a weighted average. The pump leak error was partially cancelled, since the flow rate was held constant throughout the test, and the calibration gases were run using the same arrangement and flow rate. However, the true flow rate of the sample was so low that a significant delay time appeared in the instrument response. Due to temperature changes of the exposed instrument, the instrument drift was sometimes very high (about 50 ppm over 3 hr).

Table 6. SUMMARY OF RESULTS, MRI'S CONTINUOUS CO MONITOR

Run 1A - 330 ppm		Run 1B - 451 ppm
Run 2A - 314 ppm		Run 2B - 398 ppm
Run 3A - 222 ppm	Ascarite problems	Run 3B - 489+ ppm Off scale 7 min
Run 4A - 282 ppm		Run 4B - 540 ppm
Run 5A - 292+ ppm	Off scale 4 min	Run 5B - 569+ ppm Off scale 5 min
Run 6A - 262 ppm	Ascarite problems	Run 6B - 527 ppm
Run 7A - 320 ppm		Run 7B - 476 ppm
Run 8A - 279 ppm		Run 8B - 520 ppm
Run 9A - 290 ppm		Run 9B - off scale 25 min
Run 10A - 329 ppm		Run 10B - 507+ ppm Off scale 8 min
Run 11A - 309 ppm		Run 11B - 653 ppm
Run 12A - 321 ppm		Run 12B - 484 ppm
Run 13A - 275 ppm		Run 13B - 463 ppm
Run 14A - 266 ppm		Run 14B - 664+ ppm Off scale 4 min
Run 15A - 286 ppm		Run 15B - 429 ppm
Run 16A - 236 ppm		Run 16B - 681 ppm
		Run 17B - 615 ppm

SECTION VII

STATISTICAL ANALYSIS OF COLLABORATORS' RESULTS

SAMPLING DATA

Although the basic design was not altered during the field test (see Section IV - Experimental Design), some of the data were necessarily discarded as discussed below.

Collaborator 7 demonstrated much less stable results than all other collaborators. This was not due to one or a few outliers, but instead to a genuinely more erratic performance than the other collaborators. Therefore, this collaborator was eliminated from the data analysis* after it was shown that the variance of his readings was significantly greater than the variance of other collaborators ($F_{28,31} = 2.43$).

The first three runs (Block 1) were under negative pressure, and the results reflect this undesirable fact. So the main analysis of variance deletes these three runs (they were analyzed separately); i.e., there are now 13 levels of L within Block 1, and 16 levels of L within Block 2.

Finally, on Levels 4 to 14 (Block 1), Collaborators 2 and 5 used a CO_2 correction method that was subsequently abandoned. Therefore, these 22 observations of corrected CO were calculated using the average CO_2 readings of the collaborators who made an Orsat-type analysis for CO_2. (In the uncorrected data set, this was, of course, not necessary.)

The analyses of variance (corrected and uncorrected readings) are shown in Tables 7 and 8.

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* For completeness, the analyses of variance with Collaborator 7 included are shown in Appendix D.

Table 7. AOV UNCORRECTED CO READINGS (ppm)

Source	df	SS	MS	F
C	5	142,487.49	28,497.50	19.60
B	1	1,893,348.15	1,893,348.15	49.79*
CB	5	17,652.38	3,530.48	2.40
L	27	970,660.48	35,950.39	24.76
LC	135	196,295.11	1,454.04	

* These are pseudo F-tests, since no direct F-ratio is available for testing the significance of B.

Table 8. AOV CORRECTED CO READINGS (ppm)

Source	df	SS	MS	F
C	5	96,909.06	19,381.00	15.52
B	1	1,400,344.43	1,400,344.43	50.09*
CB	5	16,010.33	3,202.07	2.56
L	27	702,166.37	26,006.16	20.82
LC	113	141,128.11	1,248.92	

* These are pseudo F-tests, since no direct F-ratio is available for testing the significance of B.

The results are quite similar whether uncorrected or corrected readings are used. There is a significant collaborator effect, and the CB interaction is also significant but small in magnitude. The "nuisance" variables, block and level, are, of course, highly significant.

The components of variance are shown in Tables 9 and 10. Thus, we see that (with $\pm$ 2 σ limits):

1. Uncorrected data

   - A collaborator will read within $\pm$ 76 ppm of his average;
   - Collaborator averages will be within $\pm$ 61 ppm of their average; and
   - A set of collaborators will read within $\pm$ 98 ppm of their average.

2. Corrected data

   - A collaborator will read within $\pm$ 71 ppm of his average;
   - Collaborator averages will be within $\pm$ 50 ppm of their average; and
   - A set of collaborators will read within $\pm$ 87 ppm of their average.

Table 9. COMPONENTS OF VARIANCE (ppm), UNCORRECTED DATA

Source	σ
$\sqrt{\sigma_e^2 + \sigma_{LC}^2}$	38.13
σ_C^2	30.54
$\sqrt{\sigma_e^2 + \sigma_{LC}^2 + \sigma_C^2}$	48.85

Table 10. COMPONENTS OF VARIANCE (ppm), CORRECTED DATA

Source	σ
$\sqrt{\sigma_e^2 + \sigma_{LC}^2}$	35.34
σ_C	25.00
$\sqrt{\sigma_C^2 + \sigma_e^2 + \sigma_{LC}^2}$	43.29

As mentioned previously, the error variance σ_e^2 and LC interaction variance are inextricable. The Kendall W Method was compared at each level for the uncorrected and corrected data sets (see Table 11).

Table 11. KENDALL W METHOD (collaborators versus level)

Data set	W	Significant?
Uncorrected, Level 1	0.656	Yes $[X^2(5) = 42.64]$
Uncorrected, Level 2	0.458	Yes $[X^2(5) = 36.67]$
Corrected, Level 1	0.658	Yes $[X^2(5) = 42.77]$
Corrected, Level 2	0.293	Yes $[X^2(5) = 23.45]$

All the concordance values are highly significant, i.e., the rank order of the collaborators is significantly preserved from level to level. However, the W values are not very close to 1, especially at the higher CO level. Thus, a significant LC interaction may very well exist.

An indirect method of decomposing $\sigma_e^2 + \sigma_{LC}^2$ and achieving an estimate of σ_e alone is shown on pages 50-51.

STANDARD ANALYSIS

Six standard samples were measured three times each by all collaborators.* Thus, the straightforward factorial model

$$X_{ijk} = \mu + L_i + C_j + LC_{ij} + e_{k(ij)}$$

was executed, where:

L_i = i^{th} (standard) level, i = 1, . . ., 6;

C_j = j^{th} collaborator, j = 1, . . ., 7;

LC_{ij} = level-collaborator interaction;

$e_{k(ij)}$ = measurement error of k^{th} observation in ij^{th} cell, k = 1, 2, 3, for every ij;

μ = overall mean;

X_{ijk} = ijk^{th} bias (collaborator reading - true).

Collaborator 7 produced results quite different from those of any other collaborator. In this case, unlike the field results, Collaborator 7 did not generate data with an anomalously large dispersion; in fact, with one exception Collaborator 7 produced identical readings at all levels of CO. However, the magnitude of this collaborator's average bias is very much larger than anyone else's; the average (overall CO levels) bias of Collaborators 1 to 6 is + 7.2 ppm, but the average bias of Collaborator 7 is + 200.9 ppm.

Therefore, Collaborator 7 was deleted from the main analysis and results are discussed in terms of Collaborators 1 through 6 only.**

The analysis of variance and components of variance estimates for the standards data are shown in Tables 12 and 13.

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* For some reason, Collaborator 6 only measured the samples twice. Thus six "missing values" were replaced in his results.

** For completeness, the standards analysis of variance including Collaborator 7 is given in Appendix D.

Table 12. AOV STANDARDS DATA

Source	df	SS	MS	F	EMS
Level	5	20,797.27	4,159.45	3.86	$\sigma_e^2 + 3\sigma_{LC}^2 + 18\sigma_L^2$
Collaborator	5	43,128.82	8,625.76	422.12	$\sigma_e^2 + 18\sigma_C^2$
LC	25	21,630.45	865.22	42.34	$\sigma_e^2 + 3\sigma_{LC}^2$
Error	66	1,348.67	20.43		σ_e^2

Table 13. COMPONENTS OF VARIANCE (ppm), STANDARDS DATA

Source	σ
Error	4.52
Collaborator	21.86
$\sqrt{\sigma_c^2 + \sigma_e^2}$	22.33

All the F-values in Table 7 are highly significant. Thus, the collaborators differ in the bias exhibited, and the (average) bias does depend upon the CO level (see Table 14). In general, a sizeable positive bias is shown at the lower CO levels, but a negative bias exists at the highest CO level. However, not all collaborators have parallel bias versus concentration curves (see Table 14).

Table 14. AVERAGE BIAS VERSUS CO CONCENTRATION

CO level (ppm)	Collaborator						
	C1	C2	C3	C4	C5	C6	A11
239	31	43	31	26	6	8	24
258	17	39	10	29	-2	-8	14
480	11	38	30	31	-21	8	16
517	5	23	20	24	-26	-7	6
734	-1	13	26	17	-49	8	3
903	-3	19	-1	-30	-110	7	-20
A11	10	29	19	16	-34	3	7

The measurement standard error (σ_e) is only 4.5 ppm; i.e., a collaborator produces readings within about ± 9 ppm of his nominal value. However, the standard error of collaborator averages is 21.9 ppm; i.e., a set of collaborator averages will be about ± 44 ppm about their center. Thus, most of the imprecision in CO readings is due to collaborator-to-collaborator variability, very little attributable to lack of repeatability.

Although the average bias is quite low, five of the six collaborators showed positive bias (in general), and the bias is definitely variable according to CO level.

COMPARISON FIELD DATA VERSUS STANDARDS DATA

In general, the standards data are more precise than the field data (see Tables 9 and 13). The "total" standard error ($\sqrt{\sigma_e^2 + \sigma_{LC}^2 + \sigma_c^2}$) is about 1-1/2 times as great in the field results as in the standards data (43.29 ppm versus 27.93 ppm). However, the standard error of collaborator means (σ_c) is about the same size in both cases (25.00 ppm, field, versus 21.86 ppm, standards). Thus, almost all of the "loss" in

precision when going from the standards data to the field data is due to increases in σ_e^2 and/or increases in σ_{LC}^2 . Unfortunately, the field data only allow the estimation of the sum of σ_e^2 and σ_{LC}^2 . In the standards data, σ_e^2 is very much smaller than σ_{LC}^2 (20.4 ppm^2 versus 281.6 ppm^2); that is, collaborators reproduce their own readings quite well at a given CO concentration, but their (average) values depend heavily on CO concentration.

A working rule of experimental design will allow us to roughly estimate σ_e^2 from the field data even though no replicates exist. If two runs, r_k and r_e, say, apparently exist at the same CO level, then the variance of their difference is theoretically $2\sigma_e^2$. In practice, many pairs of runs in the field experiment do have virtually the same CO value, because the average reading of all collaborators was nearly the same. Thus, σ_e^2 can be estimated from the field data from analyzing these paired results. Logically, of course, it is circular to simultaneously "believe" the collaborator results in order to construct pairs and then use the pairs to evaluate the reliability of the collaborators. Statistically, however, this method has produced satfactory results in many instances and has been applied to the CO data.

The result is that σ_e = 13.06 ppm (field data); i.e., the σ_e^2 + σ_{LC}^2 term is 73% LC interaction.

In summary, then, the best available estimates of components of variance are shown in Table 15.

Table 15. FIELD DATA VERSUS STANDARDS: COMPONENTS OF VARIANCE

Standard deviation (ppm)	Field	Standards
σ_e	13.06	4.52
σ_c	30.54	21.86
σ_{LC}	30.13	16.78
$\sqrt{\sigma_e^2 + \sigma_c^2}$	38.13	22.33
$\sqrt{\sigma_e^2 + \sigma_{LC}^2 + \sigma_C^2}$	48.85	27.93

SECTION VIII

CONCLUSIONS

This collaborative test comprised 16 1-hr runs at a high level nominally 500 ppm of CO, and 16 1-hr runs at a lower level nominally 300 ppm of CO, where seven different collaborative organizations sampled simultaneously according to the integrated sampling procedure given in Method 10 of the Friday, 8 March 1974 (Vol. 39, No. 47) issue of the Federal Register. These samples (two to four daily) were obtained from a manifold apparatus that was located at ground level and connected via piping to the CO boiler stack at an elevation of approximately 60 ft. In addition each collaborator took three samples from each of six cylinders of CO in nitrogen that had been supplied by the National Bureau of Standards. Several of the collaborators did not come adequately prepared to sample from the test setup. Moreover, the first few days of testing were done under extremely adverse weather conditions where heavy rains were experienced, with tornadoes in neighboring areas.

The major conclusions that can be drawn from the results of this collaborative test are:

1. Method 10 as executed in this collaborative test will produce results with only moderate accuracy of ± 87 ppm (2σ) on the average.

2. The procedures as written in Method 10 are not adequate because:

   a. The Ascarite weight gain method for measuring CO_2 content on the sample is subject to large errors due to the difficulty of measuring the small weight change obtained compared to the weight of the impinger plus the Ascarite;

b. The use of an impinger or bottle for the Ascarite trap causes great difficulties because the Ascarite tends to form a dense, solid plug in and around the glass inlet tube which, in turn, blocks the flow of the gas after a period of time;

c. Most commercial NDIR instruments have a significant amount of curvature in the calibration curves and many of the collaborators did not adequately correct for this nonlinearity of response; and

d. Some calibration gas suppliers provide certificates of analysis that show errors of as much as 30% when compared with standard gases.

SECTION IX

RECOMMENDATIONS

Based upon the conclusions that have been drawn from the results of this collaborative test, it is recommended that Method 10 be revised to cover the following points:

1. All mention of the CO_2 determination by weight gain of the Ascarite gas scrubber should be deleted. CO_2 analysis should be done by Method 3 (Orsat-type analysis) of the Federal Register.

2. The use of an impinger or bottle type of silica gel and Ascarite gas scrubber should be deleted. Sections of a flexible plastic pipe, capped at the ends, should be used instead. A minimum internal diameter of 2.5 cm is recommended to prevent blockage.

3. More explicit instructions on correcting for nonlinear response of the instruments is desirable.

4. Analysis procedures of some calibration gas suppliers are clearly inadequate. Reliable calibration gases might require NBS certification or a requirement that gas suppliers follow specific guidelines in their analysis of calibration gases.

APPENDIX A

METHOD 10 - DETERMINATION OF CARBON MONOXIDE
EMISSIONS FROM STATIONARY SOURCES

mixed representative grab sample of the sludge can be obtained.

The general rationale for the change in the opacity standard is presented in the discussion of opacity above. The three factors which led to this change are (1) the data, summarized in Volume 3 of the background information document, which, in the judgment of the Administrator, show that the proposed opacity standard was too restrictive and that the promulgated standard is not more restrictive than the mass standard, (2) the separately promulgated regulations which provide exemptions from opacity standards during periods of startup, shutdown, and malfunction (see FEDERAL REGISTER of October 15, 1973, 38 FR 28564), and (3) reevaluation of data and collection of new data and information which show that there is no basis for additional time exemptions.

Minor changes to the proposed version of the regulation have been made to clarify meanings and to exclude repetitive provisions and definitions which are now included in subpart A, General Provisions, and are applicable to all new source performance standards.

TEST METHODS

Test Methods 10 and 11 as proposed contained typographical errors that are now corrected in both text and equations. Some wording is changed to clarify meanings and procedures as well.

In Method 10, which is for determination of CO emissions, the term "grab sampling" is changed to "continuous sampling" to prevent confusion. The Orsat analyzer is deleted from the list of analytical equipment because a less complex method of analysis was judged sufficiently sensitive. For clarification, a sentence is added to the section on reagents requiring calibration gases to be certified by the manufacturer. Temperature of the silica gel is changed from 177°C (350°F) to 175°C (347°F) to be consistent with the emphasis on metric units as the primary units. A technique for determining the CO_2 content of the gas has been added to both the continuous and integrated sampling procedures. This technique may be used rather than the technique described in Method 3. Use of the latter technique was required in the proposed Method 10.

Method 11, which is for determination of H_2S emissions, is modified to require five midget impingers rather than the proposed four. The fifth impinger contains hydrogen peroxide to remove sulfur dioxide as an interferant. A paragraph is added specifying the hydrogen peroxide solution to be used, and the procedure description is altered to include procedures specific to the fifth impinger. The term "iodine number flask" is changed to "iodine flask" to prevent confusion.

Dated: February 22, 1974.

RUSSELL E. TRAIN,
Administrator.

Part 60, Chapter I, Title 40, Code of Federal Regulations, is amended by revising subpart A, by adding new subparts I,J,K,L,M,N, and O, and by adding Methods 10 and 11 to the Appendix, as follows:

Subpart A—General Provisions

See
60.2 Definitions.
60.3 Abbreviations.
60.4 Address.
60.6 Review of plans.
60.7 Notification and recordkeeping.
60.8 Performance tests.
60.12 Circumvention.

Subpart I—Standards of Performance for Asphalt Concrete Plants

60.90 Applicability and designation of affected facility.
60.91 Definitions.
60.92 Standard for particulate matter.
60.93 Test methods and procedures.

Subpart J—Standards of Performance for Petroleum Refineries

60.100 Applicability and designation of affected facility.
60.101 Definitions.
60.102 Standard for particulate matter.
60.103 Standard for carbon monoxide.
60.104 Standard for sulfur dioxide.
60.105 Emission monitoring.
60.106 Test methods and procedures.

Subpart K—Standards of Performance for Storage Vessels for Petroleum Liquids

60.110 Applicability and designation of affected facility.
60.111 Definitions.
60.112 Standard for hydrocarbons.
60.113 Monitoring of operations.

Subpart L—Standards of Performance for Secondary Lead Smelters

60.120 Applicability and designation of affected facility.
60.121 Definitions.
60.122 Standard for particulate matter.
60.123 Test methods and procedures.

Subpart M—Standards of Performance for Secondary Brass and Bronze Ingot Production Plants

60.130 Applicability and designation of affected facility.
60.131 Definitions.
60.132 Standard for particulate matter.
60.133 Test methods and procedures.

Subpart N—Standards of Performance for Iron and Steel Plants

60.140 Applicability and designation of affected facility.
60.141 Definitions.
60.142 Standard for particulate matter.
60.143 [Reserved]
60.144 Test methods and procedures.

Subpart O—Standards of Performance for Sewage Treatment Plants

60.150 Applicability and designation of affected facility.
60.151 Definitions.
60.152 Standard for particulate matter.
60.153 Monitoring of operations.
60.154 Test methods and procedures.

APPENDIX—TEST METHODS

Method 10—Determination of carbon monoxide emissions from stationary sources.
Method 11—Determination of hydrogen sulfide emissions from stationary sources.

AUTHORITY: Secs. 111, 114, Pub. L. 91-604 (42 U.S.C. 1857(c)(6) and (9)).

Subpart A—General Provisions

1. Section 60.2 is amended by revising paragraphs (i) and (l) and adding paragraphs (s), (t), (u), (v), and (w) as follows:

§ 60.2 Definitions.

* * * * *

(i) "Commenced" means, with respect to the definition of "new source" in section 111(a)(2) of the Act, that an owner or operator has undertaken a continuous program of construction or modification or that an owner or operator has entered into a contractual obligation to undertake and complete, within a reasonable time, a continuous program of construction or modification.

* * * * *

(l) "Standard conditions" means a temperature of 20°C (68°F) and a pressure of 760 mm of Hg (29.92 in. of Hg).

* * * * *

(s) "Reference method" means any method of sampling and analyzing for an air pollutant as described in the appendix to this part.

(t) "Equivalent method" means any method of sampling and analyzing for an air pollutant which have been demonstrated to the Administartor's satisfaction to have a consistent and quantitatively known relationship to the reference method, under specified conditions.

(u) "Alternative method" means any method of sampling and analyzing for an air pollutant which is not a reference or equivalent method but which has been demonstrated to the Administrator's satisfaction to, in specific cases, produce results adequate for his determination of compliance.

(v) "Particulate matter" means any finely divided solid or liquid material, other than uncombined water, as measured by method 5 of the appendix.

(w) "Run" means the net period of time during which an emission sample is collected. Unless otherwise specified, a run may be either intermittent or continuous within the limits of good engineering practice.

2. Section 60.3 is revised to read as follows:

§ 60.3 Abbreviations.

The abbreviations used in this part have the following meanings:

A.S.T.M.—American Society for Testing and Materials
Btu—British thermal unit
°C—degree Celsius (centigrade)
cal—calorie
CdS—cadmium sulfide
cfm—cubic feet per minute
CO—carbon monoxide
CO_2—carbon dioxide
dscm—dry cubic meter(s) at standard conditions
dscf—dry cubic feet at standard conditions
eq—equivalents
°F—degree Fahrenheit
g—gram(s)
gal—gallon(s)
g eq—gram equivalents
gr—grain(s)

compliance with the standards prescribed in § 60.92 as follows:

(1) Method 5 for the concentration of particulate matter and the associated moisture content.

(2) Method 1 for sample and velocity traverses.

(3) Method 2 for velocity and volumetric flow rate, and

(4) Method 3 for gas analysis.

(b) For Method 5, the sampling time for each run shall be at least 60 minutes and the sampling rate shall be at least 0.9 dscm/hr (0.53 dscf/min) except that shorter sampling times, when necessitated by process variables or other factors, may be approved by the Administrator.

Subpart J—Standards of Performance for Petroleum Refineries

§ 60.100 Applicability and designation of affected facility.

The provisions of this subpart are applicable to the following affected facilities in petroleum refineries: Fluid catalytic cracking unit catalyst regenerators, fluid catalytic cracking unit incinerator-waste heat boilers, and fuel gas combustion devices.

§ 60.101 Definitions.

As used in this subpart, all terms not defined herein shall have the meaning given them in the Act and in subpart A.

(a) "Petroleum refinery" means any facility engaged in producing gasoline, kerosene, distillate fuel oils, residual fuel oils, lubricants, or other products through distillation of petroleum or through redistillation, cracking or reforming of unfinished petroleum derivatives.

(b) "Petroleum" means the crude oil removed from the earth and the oils derived from tar sands, shale, and coal.

(c) "Process gas" means any gas generated by a petroleum refinery process unit, except fuel gas and process upset gas as defined in this section.

(d) "Fuel gas" means any gas which is generated by a petroleum refinery process unit and which is combusted, including any gaseous mixture of natural gas and fuel gas which is combusted.

(e) "Process upset gas" means any gas generated by a petroleum refinery process unit as a result of start-up, shut-down, upset or malfunction.

(f) "Refinery process unit" means any segment of the petroleum refinery in which a specific processing operation is conducted.

(g) "Fuel gas combustion device" means any equipment, such as process heaters, boilers and flares used to combust fuel gas, but does not include fluid coking unit and fluid catalytic cracking unit incinerator-waste heat boilers or facilities in which gases are combusted to produce sulfur or sulfuric acid.

(h) "Coke burn-off" means the coke removed from the surface of the fluid catalytic cracking unit catalyst by combustion in the catalyst regenerator. The rate of coke burn-off is calculated by the formula specified in § 60.106.

§ 60.102 Standard for particulate matter.

(a) On and after the date on which the performance test required to be conducted by § 60.8 is completed, no owner or operator subject to the provisions of this subpart shall discharge or cause the discharge into the atmosphere from any fluid catalytic cracking unit catalyst regenerator or from any fluid catalytic cracking unit incinerator-waste heat boiler:

(1) Particulate matter in excess of 1.0 kg/1000 kg (1.0 lb/1000 lb) of coke burn-off in the catalyst regenerator.

(2) Gases exhibiting 30 percent opacity or greater, except for 3 minutes in any 1 hour. Where the presence of uncombined water is the only reason for failure to meet the requirements of this subparagraph, such failure shall not be a violation of this section.

(b) In those instances in which auxiliary liquid or solid fossil fuels are burned in the fluid catalytic cracking unit incinerator-waste heat boiler, particular matter in excess of that permitted by paragraph (a)(1) of this section may be emitted to the atmosphere, except that the incremental rate of particulate emissions shall not exceed 0.18 g/million cal (0.10 lb/million Btu) of heat input attributable to such liquid or solid fuel.

§ 60.103 Standard for carbon monoxide.

(a) On and after the date on which the performance test required to be conducted by § 60.8 is completed, no owner or operator subject to the provisions of this subpart shall discharge or cause the discharge into the atmosphere from the fluid catalytic cracking unit catalyst regenerator any gases which contain carbon monoxide in excess of 0.050 percent by volume.

§ 60.104 Standard for sulfur dioxide.

(a) On and after the date on which the performance test required to be conducted by § 60.8 is completed, no owner or operator subject to the provisions of this subpart shall burn in any fuel gas combustion device any fuel gas which contains H_2S in excess of 230 mg/dscm (0.10 gr/dscf), except as provided in paragraph (b) of this section. The combustion of process upset gas in a flare, or the combustion in a flare of process gas or fuel gas which is released to the flare as a result of relief valve leakage, is exempt from this paragraph.

(b) The owner or operator may elect to treat the gases resulting from the combustion of fuel gas in a manner which limits the release of SO_2 to the atmosphere if it is shown to the satisfaction of the Administrator that this prevents SO_2 emissions as effectively as compliance with the requirements of paragraph (a) of this section.

§ 60.105 Emission monitoring.

(a) The owner or operator of any petroleum refinery subject to the provisions of this subpart shall install, calibrate, maintain, and operate monitoring instruments as follows:

(1) A photoelectric or other type smoke detector and recorder to continuously monitor and record the opacity of gases discharged into the atmosphere from the fluid catalytic cracking unit catalyst regenerator.

(2) An instrument for continuously monitoring and recording the concentration of CO_2 in gases discharged into the atmosphere from fluid catalytic cracking unit catalyst regenerators, except where the requirements of paragraph (a)(3) of this section are met.

(3) Instruments for continuously monitoring and recording firebox temperature and O_2 concentration in the exhaust gases from any incinerator-waste heat boiler which combusts the exhaust gases from a fluid catalytic cracking unit catalyst regenerator except where the requirements of paragraph (a)(2) of this section are met.

(4) An instrument for continuously monitoring and recording concentrations of H_2S in fuel gases burned in any fuel gas combustion device, except where the requirements of § 60.104(b) are met. Fuel gas combustion devices having a common source of fuel gas may be monitored at one location if sampling at this location produces results representative of the H_2S concentration in the fuel gas burned.

(5) An instrument for continuously monitoring and recording concentrations of SO_2 in the gases discharged into the atmosphere from the combustion of fuel gases except where the requirements of § 60.104(a) are met.

(b) Instruments and sampling systems installed and used pursuant to this section shall meet specifications prescribed by the Administrator and each instrument shall be calibrated in accordance with the method prescribed by the manufacturer of such instrument. The instruments shall be subjected to the manufacturer's recommended zero adjustment and calibration procedures at least once per 24-hour operating period unless the manufacturer specifies or recommends calibration at shorter intervals, in which case such specifications or recommendations shall be followed.

(c) The average coke burn-off rate (thousands of kilogram/hr) and hours of operation for any fluid catalytic cracking unit catalyst regenerator subject to § 60.102 or 60.103 shall be recorded daily.

(d) For any fluid catalytic cracking unit catalyst regenerator which is subject to § 60.102 and which utilizes an incinerator-waste heat boiler to combust the exhaust gases from the catalyst regenerator, the owner or operator shall record daily the rate of combustion of liquid or solid fossil fuels (liters/hr or kilograms/hr) and the hours of operation during which liquid or solid fossil fuels are combusted in the incinerator-waste heat boiler.

(e) For the purpose of reports pursuant to § 60.7(c), periods of excess emissions that shall be reported are defined as follows:

(1) *Opacity.* All hourly periods in which there are four or more 1-minute periods during which the average opacity

of the gases discharged into the atmosphere from any fluid catalytic cracking unit catalyst regenerator subject to § 60.102 exceeds 30 percent.

(2) *Carbon monoxide.* All hourly periods during which the average carbon monoxide concentration in the gases discharged into the atmosphere from any fluid catalytic cracking unit catalyst regenerator subject to § 60.103 exceeds 0.050 percent by volume; or any hourly period in which O_2 concentration and firebox temperature measurements indicate that the average concentration of CO in the gases discharged into the atmosphere exceeds 0.050 percent by volume for sources which combust the exhaust gases from any fluid catalytic cracking unit catalyst regenerator subject to § 60.103 in an incinerator-waste heat boiler and for which the owner or operator elects to monitor in accordance with § 60.105(a)(3).

(3) *Hydrogen sulfide.* All hourly periods during which the average hydrogen sulfide content of any fuel gas combusted in any fuel gas combustion device subject to § 60.104 exceeds 230 mg/dscm (0.10 gr/dscf) except where the requirements of § 60.104(b) are met.

(4) *Sulfur dioxide.* All hourly periods during which the average sulfur dioxide emissions discharged into the atmosphere from any fuel gas combustion device subject to § 60.104 exceed the level specified in § 60.104(b), except where the requirements of § 60.104(a) are met.

§ 60.106 Test methods and procedures.

(a) For the purpose of determining compliance with § 60.102(a)(1), the following reference methods and calculation procedures shall be used:

(1) For gases released to the atmosphere from the fluid catalytic cracking unit catalyst regenerator:

(i) Method 5 for the concentration of particulate matter and moisture content,

(ii) Method 1 for sample and velocity traverses, and

(iii) Method 2 for velocity and volumetric flow rate.

(2) For Method 5, the sampling time for each run shall be at least 60 minutes and the sampling rate shall be at least 0.015 dscm/min (0.53 dscf/min), except that shorter sampling times may be approved by the Administrator when process variables or other factors preclude sampling for at least 60 minutes.

(3) For exhaust gases from the fluid catalytic cracking unit catalyst regenerator prior to the emission control system: the integrated sample techniques of Method 3 and Method 4 for gas analysis and moisture content, respectively; Method 1 for velocity traverses; and Method 2 for velocity and volumetric flow rate.

(4) Coke burn-off rate shall be determined by the following formula:

$$R_c = 0.2982\,Q_{sd}\,(\%CO_2+\%CO)+2.088\,Q_{sd}-0.0994\,Q_{sd}\left(\frac{\%CO}{2}+\%CO_2+\%O_2\right) \text{ (Metric Units)}$$

or

$$R_c = 0.0186\,Q_{sd}\,(\%CO_2+\%CO)+0.1305\,Q_{sd}-0.0062\,Q_{sd}\left(\frac{\%CO}{2}+\%CO_2+\%O_2\right) \text{ (English Units)}$$

where:

R_c = coke burn-off rate, kg/hr (English units: lb/hr).

0.2982 = metric units material balance factor divided by 100, kg-min/hr-m³.

0.0186 = English units material balance factor divided by 100, lb-min/hr-ft³.

Q_{sd} = fluid catalytic cracking unit catalyst regenerator exhaust gas flow rate before entering the emission control system, as determined by method 2, dscm/min (English units: dscf/min).

$\%CO_2$ = percent carbon dioxide by volume, dry basis, as determined by Method 3.

$\%CO$ = percent carbon monoxide by volume, dry basis, as determined by Method 3.

$\%O_2$ = percent oxygen by volume, dry basis, as determined by Method 3.

2.088 = metric units material balance factor divided by 100, kg-m³/m³-hr.

0.1305 = English units material balance factor divided by 100, lb-min/hr-ft³.

Q_{sd} = air rate to fluid catalytic cracking unit catalyst regenerator, as determined from fluid catalytic cracking unit control room instrumentation, dscm/min (English units: dscf/min).

0.0994 = metric units material balance factor divided by 100, kg-min/hr-m³.

0.0062 = English units material balance factor divided by 100, lb-min/hr-ft³.

(5) Particulate emissions shall be determined by the following equation:

$$R_p = (60\times10^{-6})Q_{sd}C_s \text{ (Metric Units)}$$

or

$$R_p = (8.57\times10^{-4})Q_{sd}C_s \text{ (English Units)}$$

where:

R_p = particulate emission rate, kg/hr (English units: lb/hr).

60×10^{-6} = metric units conversion factor, min-kg/hr-mg.

8.57×10^{-4} = English units conversion factor, min-lb/hr-gr.

Q_{sd} = volumetric flow rate of gases discharged into the atmosphere from the fluid catalytic cracking unit catalyst regenerator following the emission control system, as determined by Method 2, dscm/min (English units: dscf/min).

C_s = particulate emission concentration discharged into the atmosphere, as determined by Method 5, mg/dscm (English units: gr/dscf).

(6) For each run, emissions expressed in kg/1000 kg (English units: lb/1000 lb) of coke burn-off in the catalyst regenerator shall be determined by the following equation:

$$R_e = 1000\,\frac{R_p}{R_c} \text{ (Metric or English Units)}$$

where:

R_e = particulate emission rate, kg/1000 kg (English units: lb/1000 lb) of coke burn-off in the fluid catalytic cracking unit catalyst regenerator.

1000 = conversion factor, kg to 1000 kg (English units: lb to 1000 lb).

R_p = particulate emission rate, kg/hr (English units: lb/hr).

R_c = coke burn-off rate, kg/hr (English units: lb/hr).

(7) In those instances in which auxiliary liquid or solid fossil fuels are burned in an incinerator-waste heat boiler, the rate of particulate matter emissions permitted under § 60.102(b) must be determined. Auxiliary fuel heat input, expressed in millions of cal/hr (English units: Millions of Btu/hr) shall be calculated for each run by fuel flow rate measurement and analysis of the liquid or solid auxiliary fossil fuels. For each run, the rate of particulate emissions permitted under § 60.102(b) shall be calculated from the following equation:

$$R_a = 1.0 + \frac{0.18\,H}{R_c} \text{ (Metric Units)}$$

or

$$R_a = 1.0 + \frac{0.10\,H}{R_c} \text{ (English Units)}$$

where:

R_a = allowable particulate emission rate, kg/1000 kg (English units: lb/1000 lb) of coke burn-off in the fluid catalytic cracking unit catalyst regenerator.

1.0 = emission standard, 1.0 kg/1000 kg (English unit: 1.0 lb/1000 lb) of coke burn-off in the fluid catalytic cracking unit catalyst regenerator.

0.18 = metric units maximum allowable incremental rate of particulate emissions, g/million cal.

0.10 = English units maximum allowable incremental rate of particulate emissions, lb/million Btu.

H = heat input from solid or liquid fossil fuel, million cal/hr (English units: million Btu/hr).

R_c = coke burn-off rate, kg/hr (English units: lb/hr).

(b) For the purpose of determining compliance with § 60.103, the integrated sample technique of Method 10 shall be used. The sample shall be extracted at a rate proportional to the gas velocity at a sampling point near the centroid of the duct. The sampling time shall not be less than 60 minutes.

(c) For the purpose of determining compliance with § 60.104(a), Method 11 shall be used. When refinery fuel gas lines are operating at pressures substantially above atmospheric, the gases sampled must be introduced into the sampling train at approximately atmospheric pressure. This may be accomplished with a flow control valve. If the line pressure is high enough to operate the sampling train without a vacuum pump, the pump may be eliminated from the sampling train. The sample shall be drawn from a point near the centroid of the fuel gas line. The minimum sampling time shall be 10 minutes and the minimum sampling volume 0.01 dscm (0.35 dscf) for each sample. The arithmetic average of

which necessitated by process variables or other factors, may be approved by the Administrator. A cycle shall start at the beginning of either the scrap preheat or the oxygen blow and shall terminate immediately prior to tapping.

Subpart O—Standards of Performance for Sewage Treatment Plants

§ 60.150 Applicability and designation of affected facility.

The affected facility to which the provisions of this subpart apply is each incinerator which burns the sludge produced by municipal sewage treatment facilities.

§ 60.151 Definitions.

As used in this subpart, all terms not defined herein shall have the meaning given them in the Act and in subpart A of this part.

§ 60.152 Standard for particulate matter.

(a) On and after the date on which the performance test required to be conducted by § 60.8 is completed, no owner or operator of any sewage sludge incinerator subject to the provisions of this subpart shall discharge or cause the discharge into the atmosphere of:

(1) Particulate matter at a rate in excess of 0.65 g/kg dry sludge input (1.30 lb/ton dry sludge input).

(2) Any gases which exhibit 20 percent opacity or greater. Where the presence of uncombined water is the only reason for failure to meet the requirements of this paragraph, such failure shall not be a violation of this section.

§ 60.153 Monitoring of operations.

(a) The owner or operator of any sludge incinerator subject to the provisions of this subpart shall:

(1) Install, calibrate, maintain, and operate a flow measuring device which can be used to determine either the mass or volume of sludge charged to the incinerator. The flow measuring device shall have an accuracy of ±5 percent over its operating range.

(2) Provide access to the sludge charged so that a well-mixed representative grab sample of the sludge can be obtained.

§ 60.154 Test Methods and Procedures.

(a) The reference methods appended to this part, except as provided for in § 60.8(b), shall be used to determine compliance with the standards prescribed in § 60.152 as follows:

(1) Method 5 for concentration of particulate matter and associated moisture content.

(2) Method 1 for sample and velocity traverses.

(3) Method 2 for volumetric flow rate, and

(4) Method 3 for gas analysis.

(b) For Method 5, the sampling time for each run shall be at least 60 minutes and the sampling rate shall be at least 0.015 dscm/min (0.53 dscf/min), except that shorter sampling times, when necessitated by process variables or other factors, may be approved by the Administrator.

(c) Dry sludge charging rate shall be determined as follows:

(1) Determine the mass (S_w) or volume (S_v) of sludge charged to the incinerator during each run using a flow measuring device meeting the requirements of § 60.153(a)(1). If total input during a run is measured by a flow measuring device, such readings shall be used. Otherwise, record the flow measuring device readings at 5-minute intervals during a run. Determine the quantity charged during each interval by averaging the flow rates at the beginning and end of the interval and then multiplying the average for each interval by the time for each interval. Then add the quantity for each interval to determine the total quantity charged during the entire run, (S_w) or (S_v).

(2) Collect samples of the sludge charged to the incinerator in non-porous collecting jars at the beginning of each run and at approximately 1-hour intervals thereafter until the test ends, and determine for each sample the dry sludge content (total solids residue) in accordance with "224 G. Method for Solid and Semi-solid Samples." *Standard Methods for the Examination of Water and Wastewater*, Thirteenth Edition, American Public Health Association, Inc., New York, N.Y., 1971, pp. 539–41, except that:

(i) Evaporating dishes shall be ignited to at least 103° C rather than the 550° C specified in 224 G (1).

(ii) Determination of volatile residue, 224 G (2) (b) may be deleted.

(iii) The quantity of dry sludge per unit sludge charged shall be determined in terms of either R_{vv} (metric units: mg dry sludge/liter sludge charged or English units: lb/ft³) or R_{ww} (metric units: mg dry sludge/mg sludge charged or English units: lb/lb).

(3) Determine the quantity of dry sludge per unit sludge charged in terms of either R_{vv} or R_{ww}.

(i) If the volume of sludge charged is used:

$$S_D = (60 \times 10^{-6}) \frac{R_{vv} S_v}{T} \text{ (Metric Units)}$$

or

$$S_D = (0.06) \frac{R_{vv} S_v}{T} \text{ (English Units)}$$

where:

S_D = average dry sludge charging rate during the run, kg/hr (English units: lb/hr).
R_{vv} = average quantity of dry sludge per unit volume of sludge charged to the incinerator, mg/l (English units: lb/ft³).
S_v = sludge charged to the incinerator during the run, m³ (English units: gal).
T = duration of run, min (English units: min).
60×10^{-6} = metric units conversion factor, $kg \cdot min/l \cdot hr$.
0.06 = English units conversion factor, ft³-min/gal-hr.

(ii) If the mass of sludge charged is used:

$$S_D = (60) \frac{R_{ww} S_w}{T} \text{ (Metric or English Units)}$$

where:

S_D = average dry sludge charging rate during the run, kg/hr (English units: lb/hr).
R_{ww} = average ratio of quantity of dry sludge to quantity of sludge charged to the incinerator, mg/mg (English units: lb/lb).
S_w = sludge charged during the run, kg (English units: lb).
T = duration of run, min (Metric or English units).
60 = conversion factor, min/hr (Metric or English units).

(d) Particulate emission rate shall be determined by:

$$e_{sw} = c_{sw} Q_s \text{ (Metric or English Units)}$$

where:

e_{sw} = particulate matter mass emissions, mg/hr (English units: lb/hr).
c_{sw} = particulate matter concentration, mg/m³ (English units: lb/ft³).
Q_s = volumetric stack gas flow rate, dscm/hr (English units: dscf/hr). Q_s and c_{sw} shall be determined using Methods 2 and 5, respectively.

(e) Compliance with § 60.152(a) shall be determined as follows:

$$C_{sa} = (10^{-6}) \frac{e_{sw}}{S_D} \text{ (Metric Units)}$$

or

$$C_{sa} = (2.205) \frac{e_{sw}}{S_D} \text{ (English Units)}$$

where:

C_{sa} = particulate matter emissions, kg dry sludge/kg dry sludge (English units: lb/ton dry sludge).
10^{-6} = metric conversion factor, kg/mg.
2.205 = English conversion factor, lb/kg.

9. Methods 10 and 11 are added to the appendix as follows:

Method 10—Determination of Carbon Monoxide Emissions from Stationary Sources

1. *Principle and Applicability.*

1.1 *Principle.* An integrated or continuous gas sample is extracted from a sampling point and analyzed for carbon monoxide (CO) content using a Luft-type nondispersive infrared analyzer (NDIR) or equivalent.

1.2 *Applicability.* This method is applicable for the determination of carbon monoxide emissions from stationary sources only when specified by the test procedures for determining compliance with new source performance standards. The test procedure will indicate whether a continuous or an integrated sample is to be used.

2. *Range and Sensitivity.*

2.1 *Range.* 0 to 1,000 ppm.

2.2 *Sensitivity.* Minimum detectable concentration is 20 ppm for a 0 to 1,000 ppm span.

3. *Interferences.* Any substance having a strong absorption of infrared energy will interfere to some extent. For example, discrimination ratios for water (H_2O) and carbon dioxide (CO_2) are 3.5 percent H_2O per 7 ppm CO and 10 percent CO_2 per 10 ppm CO, respectively, for devices measuring in the 1,500 to 3,000 ppm range. For devices meas-

...in the 0 to 100 ppm range. Into-service ... can be as high as 3.5 percent H2O per ... ppm CO and 10 percent CO per 50 ppm ... The use of silica gel and a caustic trap ... cifically the major interference gases. The measured gas volume must be ... corrected if these traps are used.

4. *Precision and accuracy.*

4.1 *Precision.* The precision of most NDIR ... is approximately ±2 percent of ...

4.2 *Accuracy.* The accuracy of most NDIR ... is approximately ±5 percent of ... after calibration.

5. *Apparatus.*

5.1 *Continuous sampler* (Figure 10-1).

5.1.1 *Probe.* Stainless steel or sheathed ... glass, equipped with a filter to remove ... particulate matter.

5.1.2 *Air-cooled condenser or equivalent.* To remove any excess moisture.

5.2 *Integrated sample* (Figure 10-2).

5.2.1 *Probe.* Stainless steel or sheathed Pyrex glass, equipped with a filter to remove particulate matter.

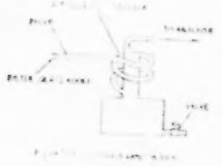
5.2.2 *Air-cooled condenser or equivalent.* To remove any excess moisture.

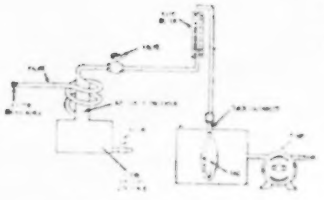
5.2.3 *Valve.* Needle valve, or equivalent, to adjust flow rate.

5.2.4 *Pump.* Leak-free diaphragm type, or equivalent, to transport gas.

5.2.5 *Rate meter.* Rotameter, or equivalent, to measure a flow range from 0 to 1.0 liter per min (0.035 cfm).

5.2.6 *Flexible bag.* Tedlar, or equivalent, with a capacity of 60 to 90 liters (2 to 3 ft³). Leak-test the bag in the laboratory before using by evacuating bag with a pump followed by a dry gas meter. When evacuation is complete, there should be no flow through the meter.





5.2.7 *Pitot tube.* Type S, or equivalent, attached to the probe so that the sampling rate can be regulated proportional to the stack gas velocity when velocity is varying with the time or a sample traverse is conducted.

5.3 *Analysis* (Figure 10-3).

5.3.1 *Carbon monoxide analyzer.* Nondispersive infrared spectrometer, or equivalent. This instrument should be demonstrated, preferably by the manufacturer, to meet or exceed manufacturer's specifications and those described in this method.

5.3.2 *Drying tube.* To contain approximately 200 g of silica gel.

5.3.3 *Calibration gas.* Refer to paragraph 6.1.

5.3.4 *Filter.* As recommended by NDIR manufacturer.

5.3.5 *CO2 removal tube.* To remove approximately 900 g of ascarite.

5.3.6 *Ice bath.* For ascarite and silica gel tubes.

5.3.7 *Valve.* Needle valve, or equivalent, to adjust flow rate.

5.3.8 *Rate meter.* Rotameter or equivalent to measure gas flow rate of 0 to 1.0 liter per min (0.035 cfm) through NDIR.

5.3.9 *Recorder (optional).* To provide permanent record of NDIR readings.

6. *Reagents.*

6.1 *Calibration gases.* Known concentration of CO in nitrogen (N_2) for instrument span, pre-purified grade of N_2 for zero, and two additional concentrations corresponding approximately to 60 percent and 30 percent span. The span concentration shall not exceed 1.5 times the applicable source performance standard. The calibration gases shall be certified by the manufacturer to be within ±2 percent of the specified concentration.

6.2 *Silica gel.* Indicating type, 6 to 16 mesh, dried at 175° C (347° F) for 2 hours.

6.3 *Ascarite.* Commercially available.

7. *Procedure.*

7.1 *Sampling.*

7.1.1 *Continuous sampler.* Assemble the equipment as shown in Figure 10-1 (or equivalent) and leak-test the sampling line. Connect the probe to the stack at a sampling point selected according to Method 1 and begin sampling at the rate proportional to the stack velocity. Allow 5 minutes for the system to stabilize then record the initial reading as required by the test procedure (see 7.2 and 8). CO content of the gas may be determined by using the Method 3 integrated sample procedure (36 FR 24886), or by using the separate CO removal tube and computing CO concentration from the gas volume sampled and the weight gain of the tube.

7.1.2 *Integrated sampling.* Evaluate the flexible bag for use by setting up the equipment as shown in Figure 10-2 with the bag disconnected. Purge the probe and sample line and ensure that all connections are leak-free. Sample at a rate proportional to the stack velocity. CO content of the gas may be determined by using the Method 3 integrated sample procedure (36 FR 24886), or by weighing the separate CO removal tube and computing CO concentration from the gas volume sampled and the weight gain of the tube.

7.2 *CO Analysis.* Assemble the apparatus as shown in Figure 10-3, calibrate the instrument, and perform other required operations as described in paragraph 8. Purge analyzer with N_2 (zero calibration). Then purge with the sample stream (span calibration) and adjust the rate to the value established for the test period. Recording the readings. Check the zero and span again after the test to assure that any drift or malfunction is detected. Record the sample data on Table 10-1.

8. *Calibration.* Assemble the apparatus according to Figure 10-3. Generally an instrument requires a warm-up period before stability is obtained. Follow the manufacturer's instructions for specific procedure. Allow a minimum time of one hour for warm-up. During this time check the sample conditioning apparatus (i.e., filter, condenser, drying tube, and CO_2 removal tube, to ensure that each component is in good operating condition. Zero and calibrate the instrument according to the manufacturer's procedures using, respectively, nitrogen and the calibration gases.

TABLE 10-1.—*Field data*

Location ..... Comments:
Test .....
Date .....
Operator .....

Clock time	*Rotameter setting, liters per minute (cubic feet per minute)*

9. *Calculation—Concentration of carbon monoxide.* Calculate the concentration of carbon monoxide in the stack using equation 10-1.

$$C_{CO_{STACK}} = C_{CO_{NDIR}}(1 - F_{CO_2}) \qquad \text{Equation 10-1}$$

where:

$C_{CO_{STACK}}$ = concentration of CO in stack, ppm by volume (dry basis),

$C_{CO_{NDIR}}$ = concentration of CO measured by NDIR analyzer, ppm by volume (dry basis),

F_{CO_2} = volume fraction of CO_2 in sample, i.e., percent CO_2 from Orsat analysis divided by 100.

[1] Mention of trade names or specific products does not constitute endorsement by the Environmental Protection Agency.

[illegible]

[illegible]

[illegible]

APPENDIX B

REQUEST FOR PROPOSAL SENT TO CANDIDATE COLLABORATORS
FOR THE METHOD 10 COLLABORATIVE TEST

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SCOPE OF WORK

I. Purpose

The purpose of this task is to provide the Environmental Protection Agency (EPA) with data on the reliability and bias of "Method 10, Determination of Carbon Monoxide Emissions from Stationary Sources." (A copy of a write-up of this method, pages 9319-9321 of the Federal Register, Vol. 39, No. 47--Monday, March 8, 1974 is attached.)

II. Statement of Work

A collaborative test program will be undertaken to achieve the purpose given in Section I above. Midwest Research Institute (MRI), as prime contractor under Contract No. 68-02-1098, will coordinate the testing, analyze the results of the collaborators, and report findings to EPA. Testing will be done simultaneously by all collaborators at the same sampling location at a specific test site. This testing will be done according to a specific experimental design made by MRI.

III. Collaborators

A. Qualifications

Each collaborator is required to provide MRI with it qualifications to do the required testing and reporting. These qualifications include:

1. Capabilities and experience of personnel who do the work;

2. Management's interest in the work;

3. Field equipment that will be used in the field on this project; and

4. Past and current programs or jobs of your company in which Carbon Monoxide (CO) was measured from stationary-source emissions and in the ambient air.

B. Project Personnel

The people who will be assigned to do this work should be identified by name. A biographical sketch of each should be given that

includes capabilities and experience that is directly related to the work task. Each person's function on the project should also be given, as well as his position on your staff.

C. Managements Interest

This should include a statement by management on its ability to furnish all the equipment that is required and that it can meet the work requirements.

D. Equipment

Each collaborator is to furnish all equipment (Figures 10-2 and 10-3 on page 9320 of the above-referred Federal Register) that is required to perform the field testing in accordance with Method 10, using the integrated gas-sampling procedure. The type (manufacture and model) and amount of this equipment that will be taken to the field for use there on this test should be identified. The recorder (Section 5.3.9 on page 9320 of above-referred Federal Register) will be required to provide permanent records of NDIR readings. Preconditioning equipment requirements specified by the NDIR instrument manufacturer must be met.

E. Company's Experience in CO Measurement

Information given should be that which is directly related to the work task of the program (current and past programs). The summary of each program cited should include the names of those project personnel (Section III.B of this RFP) who worked on it.

IV. Plan of Test

A. Number of Collaborators

Ten collaborators will be needed for this test--five to use the continuous--sampling techniques (Section 7.1.1 on page 9320 of the above-referred Federal Register), and five to use the integrated-sampling technique (Section 7.1.2 also on page 9320). However, each collaborator should be prepared to sample according to the integrated, gas-sampling procedure. The recorder (Section 5.3.9 also on page 9320) will be required to provide permanent records of NDIR readings.

B. Test Site

The test site will be the El Dorado Refinery of the American Petrofina of Texas, which is located in El Dorado, Kansas.

C. Test Location

The test will be conducted at ground level from a sampling manifold that is connected to the CO boiler emissions stack. A representative system is shown in schematic form in Figure IV-1, which is attached.

D. Experimental Design

The goals of the test are to determine: (1) accuracy--the deviation of an individual measured value from an accepted reference level; and (2) precision--the spread between individual measured values, specified by repeatability and reproducibility. It is desirable to execute Method 10 in according to each of the two procedures stated in the Method write-up--the continuous sampling procedure and the integrated sampling procedure, and to have a design so that occasional missing data will not affect the results significantly. The design in summary is:

1. Five block of tests;

2. Two blocks in which each collaborator samples from the sampling manifold for two different levels of CO--L_1 and L_2;

3. Three blocks in which each collaborator samples from "standard tanks" (Prepared by the National Bureau of Standards) for three different levels of CO--L_1, L_2 and L_3;

4. Sampling times: 60 minutes per run. The experimental procedure will be for each of the ten collaborators to determine the CO concentration at L_1 four times a day; five collaborators using the continuous-sampling procedure, and five using the integrated, gas-sampling procedure. After four days of testing, a second level of CO will be generated, and four days of observations at L_2 will be collected.

These observations will be made by each collaborator from each of the three levels (L_1, L_2 and L_3) from the "standard tanks" both before and after the CO observations of levels L_1 and L_2 of CO from the CO boiler emissions.

E. Test Schedule

The test period in the field is to be ten, 8-hr days, assuming no delays due to process operation, weather or other possible contingencies. The general tentative schedule is:

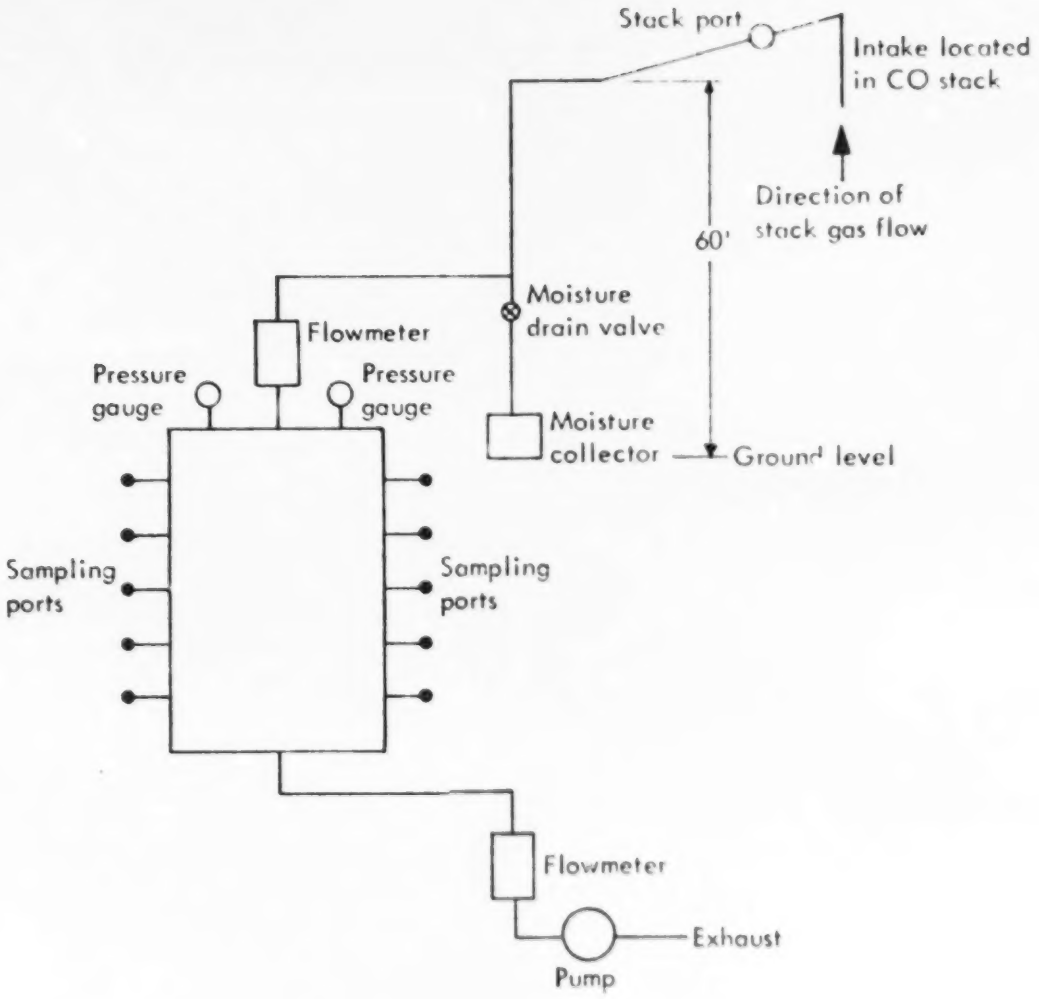

Figure B-1. On site general test setup

Day	Date	Activities
Monday	06-03-74	Orientation of collaborators, collaborator preparation for test, "standard tank" observations at levels L_1, L_2 and L_3.
Tuesday	06-04-74	Runs 1-4: sampling from manifold with CO boiler at L_1.
Wednesday	06-05-74	Runs 5-8: sampling from manifold with CO boiler at L_1.
Thursday	06-06-74	Runs 9-12: sampling from manifold with CO boiler at L_1.
Friday	06-07-74	Runs 13-16: sampling from manifold with CO boiler at L_1.
Monday	06-10-74	Runs 17-20: sampling from manifold with CO boiler at L_2.
Tuesday	06-11-74	Runs 21-24: sampling from manifold with CO boiler at L_2.
Wednesday	06-12-74	Runs 25-28: sampling from manifold with CO boiler at L_2.
Thursday	06-13-74	Runs 29-32: Sampling from manifold with CO boiler at L_2.
Friday	06-14-74	"Standard tank" observations at levels L_1, L_2, and L_3; dismantling of test set-up. Test completed.

F. Field Data Sheets

These forms will be furnished by MRI for recording all pertinent field data. A copy of each completed data sheet of a collaborator is to be given to MRI after the completion of a day's testing.

V. Summary Report

Eight copies of a summary report are to be submitted to MRI attention Paul C. Constant, Jr., within 3 weeks from the completion

of field testing. This report should not be elaborate in any way, but should include: (1) field data, (2) calculated results, (3) a discussion on how these results were obtained, (4) a discussion covering problem areas encountered in testing, explanations of data and procedures that you believe are germane to a reader's understanding of your work, and pros and cons on the write-up of Method 10, (5) a description of the field equipment you used in field sampling, giving type, manufacturer, model etc.; and (6) identification of the project team, including each person's responsibility and areas of participation.

APPENDIX C

INSTRUCTIONS FOR COLLABORATORS
CO COLLABORATIVE TEST
EL DORADO, KANSAS

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GENERAL INFORMATION

1. Calibration, sampling, analysis, etc., should be done explicitly as stated in the 8 March 1974 version of Method 10 analysis for Performance Standards for Petroleum Refineries. A permanent recorder output is required for this test. The probe and Pitot tubes will not be used. Connection of the sampling lines shall be made directly to the sampling manifold.

2. Each collaborator will be assigned a port number.

3. Code numbers for each sample will be assigned by the test supervisor. The code numbers will consist of a run number (1-2), followed by port number (1-10), followed by level designation (A or B), terminated by a collaborator number (1-7). These code numbers should appear on the recorder charts for each sample.

Collaborator	I.D.*
Scott Research	
Interpoll, Inc.	
TRW	
Environmental Triple S	
Ecology Audits	
Coors	
Entropy Environmentalists, Inc.	

4. The results for each day's runs should be given to the test supervisor at the end of each day.

5. Each collaborator should work independently of each other collaborator.

6. The morning of 3 June will be spent setting up equipment and during the afternoon a series of check gases supplied by the National Bureau of Standards will be analyzed by all collaborators. For these tests only the continuous mode test will be used.

* Omitted on purpose for this report.

7. Within 1 month of the end of test a report containing the following items shall be submitted to MRI: (a) original recorder charts, (b) calculated results, (c) a discussion on how these results were obtained, (d) a discussion covering problem areas encountered in testing, explanations of data and procedures that you believe are germane to a reader's understanding of your work, and pros and cons on the write-up of Method 10, (e) a description of the field equipment you used in field sampling, giving type, manufacturer, model, etc., and (f) identification of the project team, including each person's responsibility and areas of participation.

TEST INSTRUCTIONS

1. Prepare your equipment. The Tedlar bag with the other components of the assembly shown in Figure C-1 of Method 10* may be placed on the ground beside the sampling port. The NDIR and other equipment in Figure C-2 may be set up on the tables provided. Power outlets for both areas will be available.

2. Obtain a code number for the run.

3. Upon notification of "Start testing" from the test supervisor, connect your integrated gas train to your port and sample according to the March 1974 version of Method 10.

4. Test duration for each run will be 60 min.

5. At the signal to "Stop testing" terminate sampling and proceed immediately to analyze the sample obtained according to the method.

6. The initial flow rate with the integrated gas train shall be identical for all collaborators and will be determined by the capacity of the smallest bag. During each test you will be required to sample at a rate proportional to the flow reading from the rotameter connected to your side of the sampling manifold. A calibration curve for these meters is supplied at the end of these instructions.

7. During sample analysis the sample stream should be connected to the NDIR until a straight line of zero slope is obtained, usually no more than 10 min.

---

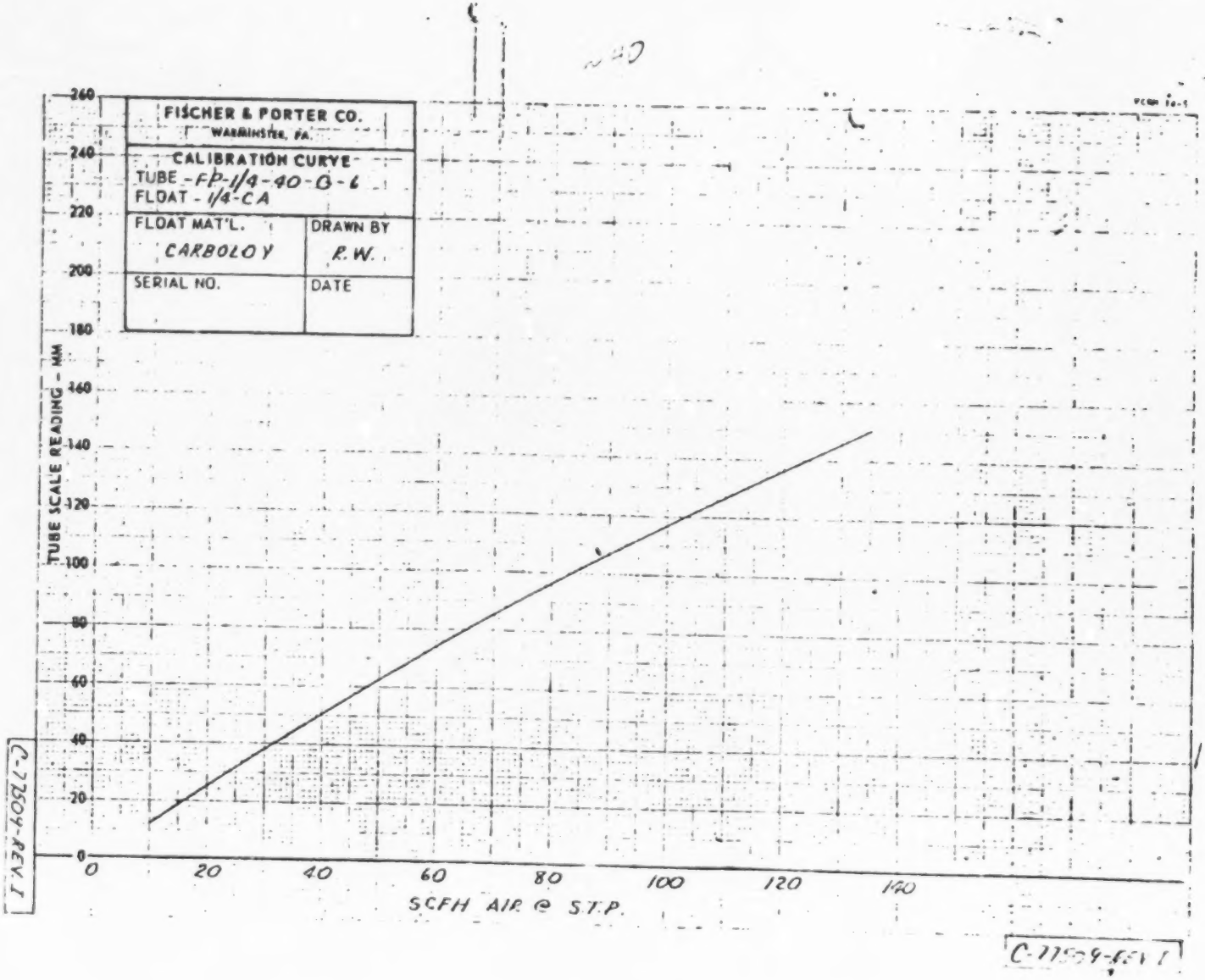
* See Appendix A for Method 10 write-up.

8. Data for each test should be recorded as shown in Table 10-1 of Method 10. All pertinent analytical data should appear on the recorder chart for each run.

9. When analysis is completed, the next run will be started after everyone is ready.

10. The tentative schedule of testing is for four runs to be made on each day. Measurements at Level A will be made 4 to 7 June, and Level B will be measured 10 to 13 June.

11. After the first day, the initial run for each day should begin at 9:00 a.m.


FISCHER & PORTER CO.
WARMINSTER, PA.
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APPENDIX D

EFFECTS OF DELETED DATA

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From the field data, one collaborator (Collaborator 7) and three levels (Runs 1 to 3, run under negative pressure) were deleted from analysis. Collaborator 7 was also deleted from the standard data. This appendix examines the reasons for these deletions and presents the analyses including the deleted data.

FIELD DATA

The pertinent changes in results arising from inclusion of Levels 1 to 3 and Collaborator 7 are shown in Table D-1. (The complete AOV's are shown in Table D-2.)

Table D-1. EFFECTS OF INCLUDING RUNS 1 TO 3 AND COLLABORATOR 7 (FIELD DATA)

		w/o Runs 1-3 (w/o Collaboratory 7)	WR 1-3
I-A.	Level mean square	26,006	38,473
	Error mean square	1,249	3,549
		w/o Collaborator 7 (w/o Runs 1-3)	WC7
II-B.	Collaborator mean square	26,006	57,270
	Error mean square	1,249	6,058

Table D-2. FIELD DATA ANALYSES OF VARIANCE

II-A. w/o Collaborator 7, w/o Runs 1-3

Source	df	ss	ms	F
C	5	96,909	19,381	15.52
B	1	1,400,344	1,400,344	437.32
CB	5	16,010	3,202	2.56
L	27	702,166	26,006	20.82
LC	113	141,128	1,249	

II-B. With Runs 1-3 added

C	5	146,244	29,249	8.24
B	1	1,170,001	1,170,001	95.88
CB	5	61,013	12,203	3.44
L	30	1,154,186	38,473	10.84
LC	122	433,019	3,549	

II-C. With Collaborator 7 added

C	6	343,619	57,270	9.45
B	1	1,524,765	1,524,765	26.21
CB	6	84,579	14,096	2.33
L	30	1,745,452	58,182	9.60
LC	133	805,732	6,058	

As seen in Table D-1, the inclusion of either Levels 1 to 3 or Collaborator 7 significantly increases the residual variation and the pertinent components of variance. In fact, the variance within Collaborator 7 is about three times greater than any other within collaborator variance. Also, 12 of the 21 observations taken on the first three runs could be labeled outliers, and two values are missing.

STANDARDS DATA

Collaborator 7 was eliminated from the standards analysis simply because Collaborator 7's bias was so great. Collaborator 7's average

bias was 30 times as great as the average bias of the other six collaborators, and an order of magnitude greater than the bias of the next most biased collaborator (see Table D-3).

Table D-3. ANALYSES OF VARIANCE (STANDARDS DATA)

III-A. w/o Collaborator 7

Source	df	ss	ms	F
C	5	43,129	8,626	422.12
L	5	20,979	4,159	4.81
CL	25	21,630	865	42.34
e	66	1,349	20.4	-

III-B. With Collaborator 7 added

C	6	621,749	103,625	5,921.4
L	5	5,047	1,009	< 1
CL	30	146,236	4,875	278.57
e	78	1,365	17.5	-

PB-241284

E R R A T A

COLLABORATIVE STUDY OF METHOD 10--
REFERENCE METHOD FOR DETERMINATION
OF CARBON MONOXIDE EMISSIONS FROM STATIONARY SOURCES--
REPORT OF TESTING

ENVIRONMENTAL MONITORING SERIES
EPA Report No. EPA-650/4-75-001

EPA Contract No. 68-02-1098
ROAP No. 26AAG
Program Element No. 1HA327
MRI Project No. 3814-C

Page 1 Fourth paragraph, Line 3, should read ...

· The within-collaborator standard deviation (σ_e) is about 12 ppm.*

Page 1 Footnote, Line 3, should read ... result in σ_e = 12 ppm.

Page 46 Table 9, Line 3, should read ... σ_c 30.54

Page 51 Second Paragraph, should read ...

The result is that σ_e = 12.29 ppm (field data); i.e., the $\sigma^2_e + \sigma^2_{LC}$ term is 73% LC interaction.

Page 51 Table 15, should read ...

Standard Deviation (ppm)	Field	Standards
σ_e	12.29	4.52
σ_c	25.00	21.86
σ_{LC}	33.13	16.78
$\sqrt{\sigma_e^2 + \sigma_c^2}$	27.86	22.33
$\sqrt{\sigma_e^2 + \sigma_{LC}^2 + \sigma_c^2}$	43.29	27.93

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